COMBUSTION SYNTHESIS OF SILICON NITRIDE / SILICON CARBIDE COMPOSITE MATERIALS

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ABSTRACT

Many nonoxide ceramic materials can be synthesized economically and with high purity by a combustion technique. Even complex solid solution, based on silicon nitride structure, could be synthesized by a direct high pressure nitridation of silicon in the presence of other oxides or nitrides. These important materials find application in manufacturing of engine parts, high performance bearings, and cutting tools. This paper focuses on in-situ synthesis of silicon nitride – silicon carbide composites. Silicon carbide/silicon nitride composites exhibit good wear and thermal shock resistance. In this research silicon carbide/silicon nitride composites were synthesized using chemically-assisted combustion technique. During that process composites were formed from elemental silicon and carbon powders in the presence of nitrogen and poly-fluorinated ethylene (teflon). Silicon nitride/silicon carbide composites with the amount of silicon carbide phase varying from 5 to 25 wt% were synthesized using this method. By altering combustion conditions it was possible to synthesize composites with different content of alpha and beta silicon nitride phases. Alteration of those conditions has also a significant effect on average particle size of synthesized composite powders. The effect of silicon carbide composition in combustion synthesized composites on microstructure is presented as well.

Keywords
Chemically enhanced combustion synthesis, Si₃N₄, SiC/Si₃N₄ composites, teflon, ammonium bifluoride.

INTRODUCTION

Silicon nitride/silicon carbide composite materials have their major application as refractory material and as material for structural application (Richerson 2000, Weimer 1997, Weinstein 1991) as automotive valves, high performance bearings, and cutting tools. These materials exhibit a great corrosion resistance and stable mechanical properties at elevated temperatures. Conventionally, these materials are produced in a reaction sintering process (Eckstroem1993). In the 90’s some researchers (Agrafiotis et al. 1991, Puszyn-
ski and Miao 1998) did some pioneering work in the field of the formation of silicon carbide by combustion synthesis. Combustion synthesis can be described as a class of highly exothermic reaction, which become self-sustaining once they are locally ignited by an external force (Liebig and Puszynski 1997, Varma et al. 1998). In the case of non oxide ceramic such as TiC, TiN, AlN, Si₃N₄, BN, this synthesis process has proven to be highly effective due to its energy costs, and high purity of the product.

The combustion synthesis of silicon carbide is a two-step process. First Si₃N₄ is formed by combustion of silicon at elevated nitrogen pressure. Then, in the presence of both Si₃N₄ and carbon, the formation of SiC took place. According to the SiC/Si₃N₄ equilibrium diagram, depicted in Figure 1, the SiC/Si₃N₄ equilibrium depends on the temperature and the gas pressure. The morphology and the phase content of both SiC and Si₃N₄ can also be controlled by the amount of halide additives such as NH₄HF₂, NH₄F, NH₄Cl, and teflon. This deliberate use of additives during the formation process is called chemical enhanced combustion synthesis. This research paper focuses on recent developments in the field of combustion synthesis of SiC, Si₃N₄, and SiC/Si₃N₄ composites.

### EXPERIMENTAL PROCEDURE

The combustion synthesis experiments were carried out in a high pressure reactor (see Figure 2). The reaction mixture was placed in a refractory boat and ignited with a resistively heated molybdenum wire. The detailed setup can be found elsewhere (Puszynski and Miao 1999).

The raw materials used were supplied from the following sources. Silicon powder (avg. particle size 7 µm) was provided by Elkem Corp. Ammonium bifluoride and teflon were purchased from Alpha Ae-Sar. Silicon nitride was ob-
tained from Starck (M11). The carbon powder was Carbon Black from Raven Corp. A silicon – silicon nitride mixture with a weight ratio 1:1 was prepared. The amount of ammonium bifluoride added to the reactant mixture varied between 1 wt% and 5 wt%. In order to synthesize the Si₃N₄/SiC composite powders, reactant mixtures consisting of silicon and silicon nitride, in the weight ratio 1:1, were mixed with 5 wt% carbon and a variable amount of teflon (2.5, 5, 10, 20 wt%).

RESULTS AND DISCUSSION

The equilibrium diagram (equilibrium composition (mol %) versus temperature) of the silicon nitrogen system without additives was generated by using HSC-thermodynamic database software from Outokumpo Inc. (see Figure 3). Results of similar calculation with the presence of 5 wt% ammonium bifluoride is shown in Figure 4. It was also possible to determine the adiabatic combustion temperatures with respect to amount of additives. The result of those calculations is a linear decrease of the adiabatic temperature with the increasing amount of ammonium bifluoride, which is shown in Figure 5. The combustion experiments of silicon nitride with 1 wt% to 5 wt% of ammonium bifluoride as additives were carried out. The x-ray diffractograms of the combustion synthesized samples with the addition of 1 wt% and 5 wt% of the ammonium bifluoride as additive are shown below (Figs. 6 and 7). Comparing both diffractograms, it is obvious that the amount of alpha–silicon nitride increased with the amount of halide additive added. A reason for that might be the increased amount of gaseous silicon.
containing species, which form alpha silicon nitride when reacting with nitrogen. When no additives were used, like in the simulation depicted in Figure 3, it is more likely that the formation of silicon nitride takes place via liquid phase mechanism. This process favors the formation of the high temperature beta phase.

Figure 8 depicts the relation between the quantity of halide additives used and the phase content of combustion synthesized silicon nitride. The larger the amount of additives, the more alpha-Si$_3$N$_4$ can be found in the products (see Figure 8). However, if more than 5 wt% ammonium bifluoride were added to the reactant mixture, the combustion reaction was not self-propagating anymore.

In further experiments, the combustion synthesis reaction was modified to synthesize Si$_3$N$_4$/SiC composites materials. This objective was achieved by adding a small amount of carbon and poly b-fluorinated ethylene (teflon) to the silicon-nitrogen system. It should be noted that the addition of 2 wt% of carbon already had an impact on the phase content of the product. The x-ray diffractogram depicted in Figure 9 indicates that the amount of alpha silicon nitride increased to 28 wt%. When teflon was added, the beta silicon nitride phase further decreases. This can be observed in the x-ray diffractogram of the sample when 5 wt% teflon was added to the reactant mix-
ture (see Figure 10). Furthermore, when comparing the SEM–images of the samples without teflon (Fig. 11a), and with teflon (Fig. 11b), one can observe a reduction in particle size. Without teflon, an average particle size was 7 µm (Fig. 11a). The fluorine introduced to the system through teflon, reacts with the silicon and lead to the formation of smaller crystals (Fig. 11b — less than 2 µm, needle-like). Figure 12 shows a comparison of the phase content in Si₃N₄/SiC composite powders when different amounts of teflon were used in the reactant mixture. The increased amount of fluoride introduced by teflon decreases the formation beta silicon nitride by (i) enhancing gas phase reaction and (ii) by decreasing the adiabatic temperature.

CONCLUSIONS

Chemical enhanced combustion synthesis can be applied to form Si₃N₄ and SiC/Si₃N₄ with an increased amount of alpha Si₃N₄ phase. Equilibrium calculations support the mechanism of the formation of silicon nitride in the presence of ammonium bifluoride. The calculations also have shown that the adiabatic combustion temperature decreased with in-
creasing amounts of that additive. It was found experimentally that the use of ammonium bifluoride significantly effects phase content, morphology, and particle size of combustion synthesized silicon nitride based materials. The addition of teflon to silicon-nitrogen-carbon system results in the formation of the composite powder with smaller particle sizes. Also, the phase content of Si$_3$N$_4$-SiC-composite is effected by the addition of teflon. Further sintering experiments to form SiC/Si$_3$N$_4$ composite materials for structural application are underway.

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