# FORMATION OF NEAR-NANO SIZE $TiB_2$-TiN-$Al_2O_3$ POWDER BY SHS

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***Abstract:*** *Formation of $TiB_2$, TiN and $Al_2O_3$ powder mixtures were obtained through self-propagating high-temperature synthesis (SHS), starting from $TiO_2$ + BN + Al mixtures. As a diluent, NaCl was added in 0-40 wt% range to the starting mixture in order to refine the size of the formed particles. Thermochemical calculations were performed by Factsage software. The products were subjected to XRD, SEM and particle size analyses. Intended reaction products were obtained in the $TiB_2$, TiN and $Al_2O_3$ system according to XRD analyses, with no cross reaction products. The crystallite size of the products decreased with the increasing amount of NaCl according to the broadening of the peaks on the XRD patterns of the products. Particle size measurements revealed that near-nano size particles were formed. A decrease in the adiabatic temperature was calculated, a decrease in the velocity of the SHS wave front was observed and a decrease in the particle size of the obtained products was measured as a result of the increase in the diluent amount.*

**Keywords**: $TiB_2$, TiN, $Al_2O_3$, near-nano particles, SHS

## *1. Introduction*

Titanium nitride, titanium diboride and aluminum oxide are significant ceramic materials. They possess some attractive properties such as high hardness, wear and oxidation resistance and high melting points [1,2]. The attention on the ultrafine or near-nano size ceramic particles and on the sintered articles comprising of these particles is principally due to the ability of sintering at lower temperatures and to higher densities. This is achieved as a result of the increased surface area of the near-nano size powder as compared to micron-scale powder. The mechanical properties of the sintered objects comprising nano or near-nano size particles are reported to be superior [3].

In SHS, a loose pellet of reactants is formed and it is ignited on one surface. As a result of the high exothermicity of the reaction, the heat wave propagates along the pellet, until all of the reactants are consumed. SHS has some advantages as compared to other solid state synthesis methods such as mechanochemical synthesis since reactions take place in a very short time in SHS, generally cheap starting materials such as oxides are utilized, there is no need for a high temperature furnace, the heat input is very low and the method is rather easy. Carbides, nitrides and borides, as well as composite powders have been obtained by SHS previously [4-10].

In fact it is not a simple process to obtain sub-micron or near-nano size particles via SHS. This is mainly due to the fact that products reach high temperatures, which results in rapid grain growth. Utilization of diluents is a generally accepted approach in reducing the size of the formed particles by SHS. Salts, such as NaCl have been used in various studies in the literature [3].

The aim of the present study is to form TiN–$TiB_2$–$Al_2O_3$ powder mixture by SHS and to refine the grain size by addition of NaCl to the reactants.

## *2. Experimental Procedure*

Reactant mixture was composed of $TiO_2$, BN and Al powder. Amounts of the constituents of the reactant mixture were calculated according to the stoichiometry of Reaction (1). NaCl was added into the reactant mixture at amounts in 0-40 wt % range. The reaction system was subjected to thermochemical analysis with Factsage software. Possible stable phases can be predicted by this software as a function of the system variables.

$$3TiO_2 + 2BN + 4Al + X\ NaCl = TiB_2 + 2TiN + 2Al_2O_3 + X\ NaCl \quad (1)$$

The reactant mixture was mixed thoroughly in a mortar and pestle. The reactant mixture was compacted in a steel die in the form of a pellet having 10 mm diameter and about 10 mm height. The density of the pellet was about 40 % of the theoretical density. SHS experiments were conducted in a combustion chamber which was made of stainless steel.

The pellet was placed in the combustion chamber under an ignition coil which was made of Cr-Ni resistance wire. The chamber was vacuumed and then filled with argon. The ignition coil was heated rapidly with electric current and the pellet was ignited from one end. The reaction wave proceeded along the pellet until all of the reactants were converted into products. The products were ground in a mortar, NaCl was removed by dissolving in water and centrifuging, and the obtained powder was subjected to XRD, SEM and particle size analyses.

## *3. Results and Discussion*

### *3.1. Thermochemical Analyses*

The reaction system was subjected to thermochemical analyses and the adiabatic temperature of Reaction (1) was calculated as a function of NaCl diluent amount in the reactants. The results are presented in Figure 1 where the arrows indicate the investigated molar ratios of NaCl in Reaction (1).

The adiabatic temperature was 2050 $^oC$ when no NaCl was used, which is equal to the melting temperature of $Al_2O_3$. It decreased to 1490 $^oC$ when X=1.36 and it was the same for more additions of NaCl.

Possible phases in the system as a function of NaCl amount, as predicted by Factsage software are presented in Figure 2. $Al_2O_3$, TiN and $TiB_2$ are the expected reaction products. It can be seen that $Al_2O_3$ is in liquid state when no NaCl was used and up to about X=0.2 mol NaCl according to Reaction (1); and it is in solid form at higher NaCl addition amounts. NaCl is in gaseous form up to X=1.5 mole NaCl amount and then it coexists with NaCl in liquid form.

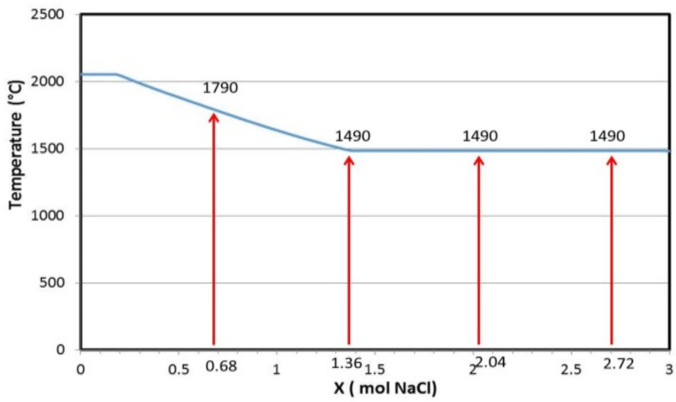


***Fig. 1*** *Adiabatic temperature of Reaction (1) as a function of NaCl amount in the reactant mixture.*

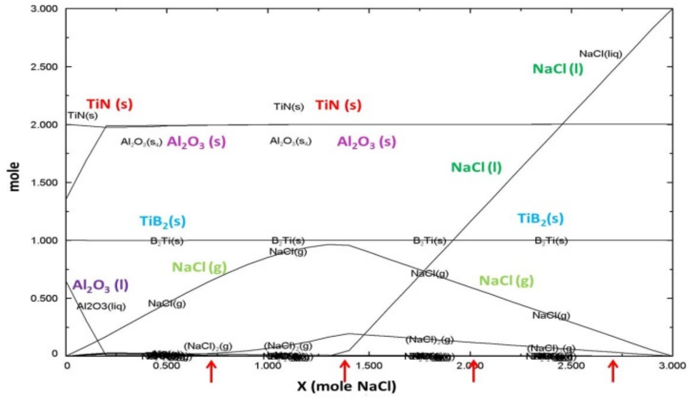


***Fig. 2*** *Possible phases in the system as a function of NaCl amount, predicted by Factsage software.*

## *3.2. XRD Analyses*

XRD patterns of the products obtained by using 10, 20, 30 and 40 wt% NaCl additions in the reactant mixture are presented in Figure 3. It can be seen that the expected reaction products were obtained with all the compositions. Mixture having NaCl addition higher than 40 wt% could not be ignited.

The peaks pertaining to $TiB_2$ and TiN broaden with increase in the NaCl amount in the reactant mixture. This indicates that the crystallite size of $TiB_2$ and TiN become smaller with the increase in the NaCl amount. On the other hand, peaks of $Al_2O_3$ seem to be not affected from the increase in NaCl amount. This may be due to lower melting point of $Al_2O_3$ as compared to $TiB_2$ and TiN.

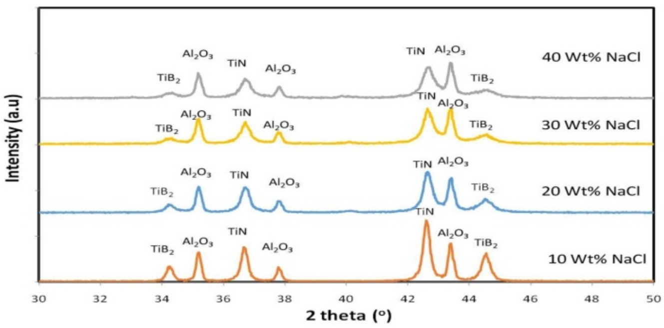


***Fig. 3*** *XRD patterns of the products obtained by using 10, 20, 30 and 40 wt% NaCl additions in the reactant mixture.*

## *3.3. SEM Examinations*

SEM micrographs of the products obtained from the mixtures containing no NaCl, 10 wt% NaCl and 40 wt% NaCl are presented in Figure 4 (a), (b) and (c), respectively. The particles in the reaction products obtained without NaCl addition are larger than those obtained with NaCl additions. It was seen that particle size decreases with increase in NaCl amount.

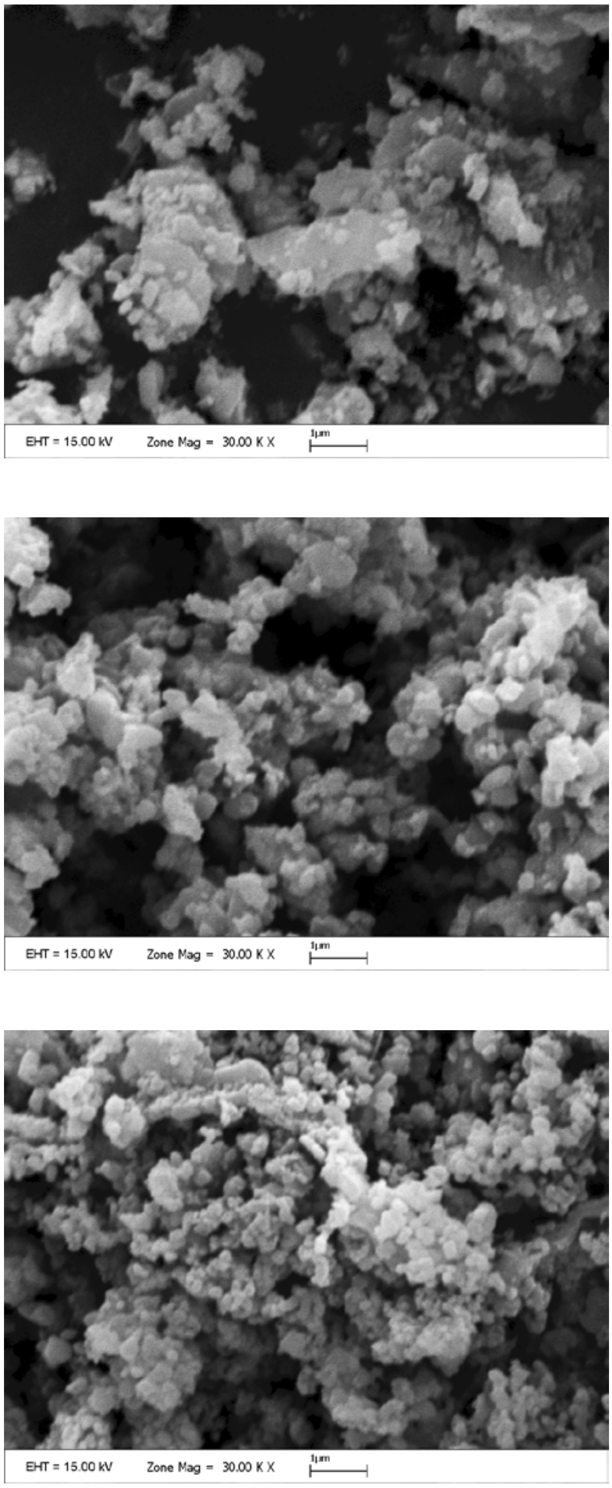


***Fig. 4*** *SEM micrographs of the products obtained from the mixtures containing (a) no NaCl, (b) 10 wt% NaCl and (c) 40 wt% NaCl.*

### *3.4. Particle Size Analysis*

Particle size distribution plot of $TiB_2$ + TiN + $Al_2O_3$ product mixture obtained from the reactant mixture containing 30 wt% NaCl is presented in Figure 5. It can be seen that almost all of the particles were smaller than 1 micrometer. Most of the particles were around 200-300 nm, indicating that they are near-nano size particles.

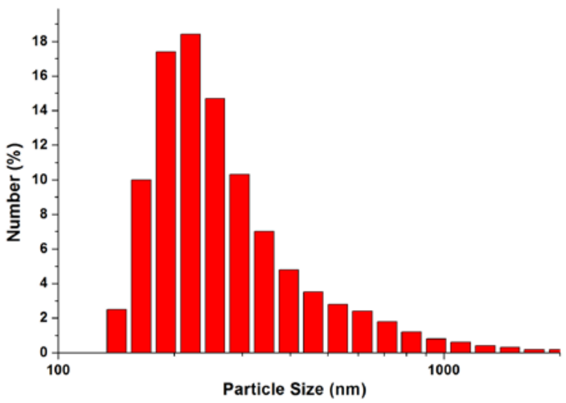


***Fig. 5*** *Particle size distribution plot of TiB2 + TiN + Al2O3 product mixture obtained from the reactant mixture containing 30 wt% NaCl.*

It was demonstrated that utilization of diluents is an effective tool for obtaining near-nano particles by SHS. Use of salts can be stated to be more advantageous than using products as diluents. The effect of NaCl in reducing the size of the formed particles in SHS may be the decrease of the attained temperature, separation of the formed particles from each other and prevention of bulk diffusion.

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