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Combustion of TiO₂–Mg and TiO₂–Mg–C systems in the presence of NaCl to synthesize nanocrystalline Ti and TiC powders

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Abstract

The combustion process of TiO_2 -Mg and TiO_2 -Mg–C systems with sodium chloride as an inert diluent was investigated. The values of combustion parameters and temperature distribution on a high-temperature wave according to the amount of sodium chloride were obtained by the thermocoupling technique. The leading stages of combustion processes are found and the sizes of reactionary zones were estimated. It is shown that the introduction of NaCl in an initial mixture promotes the formation of a nanocrystalline structure of the final products. As a result, nanosized titanium, and titanium carbide powders have been successfully obtained. \bigcirc 2003 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In recent years, much effort has been directed towards the process of development of transition metal powder and based composition (carbides, borides, nitrides, etc.) with improved morphology and nanosized particles. Various methods have been explored for their manufacturing, such as: melt crystallization, CVD, laser, carbon reduction, metallic wire explosion, self-propagating high-temperature synthesis (SHS), etc. [1–3].

Among the powder production methods, we focus our attention on the novel method known as SHS [4,5]. The advantage of the SHS method in comparison with other methods: low energy consumption for the achievement of high temperatures, high rate of synthesis, simplicity of special equipment and high quality of the final products. Nowadays, a large number of various binary and complex chemical compositions are already synthesized by the SHS method. Despite this, the synthesis of nanosized metallic powder and

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based composition is very poorly investigated. Among the few published papers, nanosized titanium carbide powder was synthesized by the SHS process from metallic titanium in our recent work [6], where NaCl was used as the particle size controlling agent. It is worthy to note that a similar phenomena was observed by R.L. Axelbaum in a sodium/halide flame. In Axelbaum's research the nanoparticles were encapsulated during synthesis, making them stable in air and monodispersed in form [7].

In this work the combustion of the systems TiO_2 -Mg and TiO_2 -Mg-C in the presence of sodium chloride were investigated with the intention of nanocrystalline Ti and TiC powder synthesis.

For the first time SH-synthesis of metallic titanium and titanium carbide powders from the TiO₂–2Mg and TiO₂–2Mg–C initial mixtures was carried out in ISMAN, Russia [8–10]. It is shown, intensive evaporation of magnesium takes place during the combustion when the pressure of the surrounding gas is low. This negatively reflected not only the degree of conversion, but also the quality of the synthesized products. For the suppression of the magnesium evaporation, the process combustion of these systems were performed under high pressure of inert gas (at $P_{Ar} = 5$ MPa). As a result Ti, MgO, and Ti, MgO containing biphase products were correspondingly formed. It is shown that after purification the dispersity of titanium and titanium carbide powders = 0.5–1 µm.

2. Experimental

The experiments were carried out in a constant pressure reactor using cylindrical pellets 30 mm in diameter and 40 mm in height in argon atmosphere at pressure of 0.5 MPa and sodium chloride contents in the initial mixture were varied from 0.2 to 1.0 mol. Experimental densities of samples were 1.2–1.3 g/cm³. The raw materials used: titanium dioxide (anatase, 99.8% purity, <1 µm), granulated black carbon (<0.1 µm), magnesium powder (chemical pure, <150 µm), sodium chloride (99.8% purity, <50 µm), and argon gas (99.9% purity). The maximum combustion temperatures (T_c) were measured by tungsten–rhenium thermocouples (W/Re – 5% versus W/Re – 20%) 100 µm in diameter previously covered with a thin layer of boron nitride and embedded in the center of the sample at predefined distances. The input signals of the thermocouple were transformed by a data logger (DASTC) at a rate of 10 Hz, and were recorded by a computer. The average values of combustion velocity are as follows: $U_c = l/t$, where U_c is the combustion velocity; l is the distance between thermocouples; t is the temporary distance between signals of thermocouples. The standard error of measurement for T_c and $U_c = \pm 50$ °C and 5%, respectively.

The crystal structure of the burned down samples were analyzed by X-ray diffractometer (Siemens D5000). The microstructure study of the end products was carried out using Field Emission Scanning Electron Microscopy (JSM 6330F) and Transmission Electron Microscope (TEM) for the observation of submicron structure.

3. Results and discussion

3.1. Thermodynamic analysis of TiO_2 –2Mg–kNaCl system. The laws of combustion and phase formation

To estimate the influence of NaCl additive content on the adiabatic combustion temperature (T_{ad}) and equilibrium composition of the final product a preliminary thermodynamic analysis of TiO₂-2Mg-kNaCl



Fig. 1. Thermodynamic calculation of adiabatic combustion temperature and equilibrium composition of products for TiO₂–2Mg-kNaCl system upon k ($P_{Ar} = 0.5$ MPa).

system (where k is mole number of NaCl) was performed by the program "THERMO" [11]. Program "THERMO" was developed for the calculation of thermodynamic equilibrium in complex multicomponent heterophase systems to analyze the possible composition of synthesized products (condensed and gaseous) and adiabatic combustion temperature of the system. Calculations of equilibrium characteristics is based on minimizing the system thermodynamic potential, which expressions account for the contributions of thermodynamic potentials for all the components present in the system, providing their concentrations.

The results of the thermodynamic calculations carried out at P = 0.5 MPa are shown in Fig. 1. As one can see, k = 0 reaction products are multiphase: Ti, MgO, TiO, and unreacted Mg. The introduction of NaCl resulted in a monotonic decrease of Mg and TiO in the combustion products. At $k \ge 0.5$, they practically disappeared from the calculated composition of products. As the adiabatic combustion temperature (T_{ad}) monotonously decreased from 1890 K (k = 0) to 1490 K (k = 1.0). The decrease of T_{ad} takes place due to the heat expenses of NaCl warming up as an inert dilutent. Thus, the results of the thermodynamic calculations directly indicate that optimum conditions for realizing the combustion process are reached at k > 0.5.

In similar conditions, the thermodynamic calculation for the experimental investigation is performed. In particular, the effect of the NaCl content on combustion temperature (T_c) , velocity (U_c) and weight loss of the sample (Δm) for the TiO₂-2Mg-kNaCl system is investigated (Fig. 2). As well as in the thermodynamic calculations, the introduction of NaCl in an initial mixture linearly decreases the combustion temperature from 1830 K (at k = 0) to 1580 K (at k = 0.92). As we can see from the Table 1, maximum differences between experimentally measured (T_c) and thermodynamically calculated temperature (T_{ad}) equal 140 °C (k = 0.54), which is quite satisfactory for SHS processes. It is also expected that T_{ad} is normally larger than T_c . However, there is one exception from this rule at k = 0.92. It may be due to a standard error of measurement.

As distinct from combustion temperature, with the increasing of k, the wave propagation velocity (U_c) drastically falls, in particular, it was observed to be ~17 times lower, when k changes from 0 to 0.92.



Fig. 2. Dependencies of T_c , U_c , and Δm upon k at combustion of TiO₂-2Mg-kNaCl system ($P_{Ar} = 0.5$ MPa).

The weight loss of the sample (Δm), which is calculated by the formula: $\Delta m = [(m_{in} - m_{fin})/m_{in}] \times 100\%$ (where, m_{in} is the initial weight of the sample, m_{fin} is the final weight of the sample), has similar to U_c decreasing character. Minimum weight loss (1–2 wt.%) was registered when $k \ge 0.5$. According to visual observation, the combustion product has a homogeneous black color on all the sections of combusted sample in this interval of k.

The typical XRD patterns of the product synthesized from the $TiO_2-2Mg-0.54NaCl$ initial mixture are given in Fig. 3. Three phases can be seen in the combustion product: MgO, Ti, and NaCl (Fig. 3a). After acid enrichment of the final product pure metallic titanium was obtained (Fig. 3b).

In order to estimate the size controlling effect of NaCl, FESEM studies of the microstructure of titanium powders were carried out. The micrographs obtained at different k are shown in Fig. 4. As is apparent at k = 0, the titanium particles display an undefined shape with an average size 0.2–1 µm. By increasing the NaCl content in the starting mixture the titanium particles are going to be smaller and uniform. It can be seen that introducing 0.24 mol of NaCl results in a noticeable decrease of Ti particle size (Fig. 4b). The increase of NaCl up to 0.54 mol causes formation of nanosized spheroidal titanium particles (Fig. 4c). The particle size estimated from this micrograph is below 100 nm. The chemical activity of powder obtained is high enough, in particular the filter paper impregnated with this powder instantly flares up scattering bright, white sparks by a weak beam of fire.

Table 1 The values of U_c , T_{ad} , and T_c for the TiO₂-2Mg-kNaCl system

k	$U_{\rm c}~({\rm cm/s})$	$T_{\rm ad}$ (K)	<i>T</i> _c (K)
0	5	1892	1830
0.24	3	1817	1800
0.54	0.5	1740	1600
0.92	0.3	1530	1580



Fig. 3. Typical XRD patterns of the final products synthesized from the TiO_2 -2Mg-0.54NaCl initial mixture: (a) after combustion, (b) after acid enrichment.

3.2. Thermodynamic analysis of $TiO_2-2Mg-C-kNaCl$ system. The laws of combustion and phase formation

The results of the preliminary thermodynamic analysis of $TiO_2-2Mg-C-kNaCl$ system are shown in Fig. 5. The absence of NaCl (k = 0) the $TiO_2-2Mg-C$ system has a rather high, calculated adiabatic combustion temperature ($T_{ad} = 2480$ K), which is connected with the titanium carbide formation. With the increase of k, T_{ad} monotonously decreases and at k = 0.55-1.0, it becomes equal to 2030 K. At the same time, positive changes take place in the calculated composition of reaction products, in particular an increase of k causes a stable decrease of TiO and Mg concentration and at k > 0.5 favorable conditions for biphase product formation are provided.

The influence of the amount of NaCl on the regularities of combustion of TiO₂-2Mg-C-kNaCl system was examined at k = 0-1. These data are plotted in Fig. 6. At $k \le 0.5$, the large weight loss of the sample (Δm) is observed because of the strong gas realized during the combustion. As a consequence, the measured values of T_c are low in comparison with T_{ad} (see Table 2).

Table 2 The values of U_c , T_{ad} , and T_c for the TiO₂-2Mg-C-kNaCl system

k	$U_{\rm c}~({\rm cm/s})$	$T_{\rm ad}$ (K)	$T_{\rm c}$ (K)
0	5	2480	2100
0.27	1.1	2250	2050
0.58	0.5	2050	2030
1	0.3	2040	1850



Fig. 4. The FESEM microstructures of the Ti powders synthesized from the TiO₂-2Mg-kNaCl mixture at: (a) k = 0; (b) k = 0.24; (c) k = 0.54.

At k > 0.5, the weight loss recorded during the combustion is minimal and equals 0.7–2.0 wt.%. In this area the combustion velocity has a stationary character and 0.3–0.5 cm/s value. At k = 0.6–0.8, T_c is going to be close to T_{ad} , which indirectly specifies the complete transformation of initial components into the final products. The visual observations have also shown that combustion products have a homogeneous black color on all section of the sample at k = 0.6–0.8.



Fig. 5. Thermodynamic calculation of adiabatic combustion temperature and equilibrium composition of products for TiO₂–2Mg–C–kNaCl system upon k ($P_{Ar} = 0.5$ MPa).

According to results of the XRD-analysis reaction, TiC, MgO and NaCl products are multiphase (Fig. 7a). After acid enrichment of the product (k = 0.58) from MgO and NaCl, monophase TiC was obtained (Fig. 7b).

The FESEM micrographs of the TiC powder obtained from the initial mixture $TiO_2-2Mg-C-kNaCl$ at different *k* are given in Fig. 8; which may be similar with the titanium decreasing tendency of the titanium carbide particles due to the amount of NaCl. In particular, at an absence of NaCl the particles of TiC are non-perfect crystals with an average size 0.2–0.5 µm (Fig. 8a). At k = 0.27, the size distribution of TiC particles are very narrow: 0.1–0.3 µm (Fig. 8b). The future increase of *k* results in the formation of TiC nanocrystal structure (Fig. 8c). The TiC particles size estimated from this



Fig. 6. Dependencies of T_c , U_c , and Δm upon k at combustion of TiO₂-2Mg-C-kNaCl system ($P_{Ar} = 0.5$ MPa).



Fig. 7. Typical XRD patterns of the end products synthesized from the $TiO_2-2Mg-C-0.58NaCl$ initial mixture: (a) after combustion, (b) after acid enrichment.

micrograph is about 30–100 nm. The main characteristics of the obtained titanium carbide is given below:

Total carbon (C_{total})—20 wt.% Free carbon (C_{free})—0.3–0.5 wt.% Lattice parameter—4.33 Å Particles size (r)—30–100 nm

3.3. Mechanism of combustion and phase formation

With regard to the above-stated factors, the chemical transformations on the combustion wave of the $TiO_2-2Mg-C-kNaCl$ system can be divided into two basic stages.

3.3.1. TiO_2 reduction stage

This is the main combustion stage of the TiO₂-2Mg-kNaCl system and the first combustion stage of the TiO₂-2Mg-C-kNaCl system. In this step, the interaction between TiO₂ and Mg occurs due to the heat expense of the igniter (in this case Ti + C). According to DTA-analysis the combustion reaction is stimulated because of the melting magnesium ($T_{meltMg} = 930$ K). The approximate scheme of TiO₂ reduction can be presented as follows:

$$Mg (solid) \to Mg (liquid)$$

$$Tio_{A} = Mg (liquid)$$

$$TiO_2 (solid) + Mg (liquid) \rightarrow Ti + MgO$$
 (2)



Fig. 8. The FESEM microstructures of the TiC powders synthesized from the TiO₂-2Mg-C-kNaCl mixture at: (a) k = 0; (b) k = 0.27; (c) k = 0.58.

The interaction of TiO₂ with Mg is accompanied by the melting of NaCl ($T_{meltNaCl} = 1080$ K). Consequently, the formation of titanium particles takes place in the NaCl melt, which protects it from agglomeration and further growth. The Ti particles surrounded by NaCl are visible in Fig. 9a; taken from the TiO₂-2Mg-0.54NaCl reaction system. Fig. 9b illustrates the microstructure of the same powder after acid enrichment. The Ti particles are crystalline in form and about 30–100 nm.



Fig. 9. TEM-images of Ti and TiC powders: (a) distribution of Ti powder in the NaCl shell; (b) microstructure of Ti powder; (c) microstructure of TiC powder.

3.4. The carbonization stage

Consequent carbonization of titanium takes place in the mixture by the reaction (3) heated by reaction (2) in post-combustion zone. Therefore, it does not considerably influence the combustion velocity.

$$Ti + C \rightarrow TiC$$
 (3)



Fig. 10. Average temperature distribution in combustion zone for TiO₂-2Mg-0.54NaCl (1) and TiO₂-2Mg-C-0.58NaCl (2) mixtures at $P_{Ar} = 0.5$ MPa.

The formation of titanium carbide particles also occurs in the NaCl melt, which provides their nanocrystal structure (Fig. 9c).

At k = 0.5-1.0 (where the measurements have high precision due to small evaporation), combustion velocity for both processes was nearly identical and recorded to be 0.3-0.5 cm/s. This means that the reduction stage is leading for all combustion. The reaction of titanium carbonization only supplements the heat power of the combustion system and does not influence, in any way, combustion velocity.

Average temperature distributions in combustion zones for TiO₂-2Mg-0.54NaCl (1) and TiO₂-2Mg-C-0.58NaCl (2) system (Fig. 10) can be very useful for the observation of the reaction mechanism. Here T_0 is the starting temperature of the sample; T^* is the starting temperature of the reaction. According to the experimental measurement, the value of T^* equals 900–950 K, which corresponds to the melting temperature of magnesium. There are two zones in this system: the heating zone (Michaelson zone) and the chemical reaction zone (L). The heating zone is located to the left side of the axis of the ordinate, and the chemical reaction zone corresponds to the right. The thickness of a heating zone, which corresponds to a change of temperature from T_0 to T^* was narrow (l = 0.4-0.5 mm) in comparison with the chemical reaction zone (L = 6-20 mm). The chemical reaction zone conditionally exists from the zone of wave propagation ($0 < x \le 2$) to the post-combustion zone (x > 2). Thus, the reaction (1), which was approximately realized in the narrow zone close to T^* was responsible for the combustion wave propagation. Reaction (2) is realized only in the post-combustion zone and in that case does not have any influence on the velocity of wave propagation.

During combustion, the melting of sodium chloride, which occurs in the heating zone $(T_{meltNaCl} = 1074 \text{ K})$, plays an important role. In particular, melted sodium chloride closes the pores of the combusting sample, interferes with evaporation of magnesium, and creates protective shells

around the titanium and titanium carbide particles. Thus, allowing them to keep not only their primary nanocrystalline structure, but also preventing possible agglomeration during high-temperature reaction.

4. Conclusion

The combustion laws of the TiO_2 -2Mg and TiO_2 -2Mg-C systems in the presence of NaCl were investigated. The thermodynamic states of systems were analyzed and the most favorable ranges for Ti and TiC synthesis were revealed.

The experimental dependencies of combustion temperature and velocity, and weight loss of samples from the amount of sodium chloride entered in an initial mixture were received. It is shown that the reduction stage is leading for the combustion process. The optimum conditions for nanocrystalline Ti and TiC powder synthesis were found.

XRD, FESEM, and TEM analyses were performed. It was shown that the nanocrystalline structure of Ti and TiC powder are formed due to protective shells of NaCl, which is formed around primary Ti and TiC particles.

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