Effect of mechanical pre-activation on the nitriding of aluminum ferrosilicon in the combustion mode

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Abstract. A ceramic β-SiAlON-based composite is obtained by the SHS method using aluminum ferrosilicon as a raw material. The effect of mechanical pre-activation of a reaction mixture on the nitriding of aluminum ferrosilicon is studied. Mechanical activation of initial powders initiates SHS reaction at lower pressures and diameters, i.e. expands the parameters of combustion of aluminum ferrosilicon in nitrogen. It is shown that the nitriding of mechanically activated powders in the combustion mode can be used to obtain products with a higher nitrogen content. The products were investigated thoroughly. XRD analysis showed the presence of major phase β-$Si_3Al_3O_3N$. As being one of the most widely used structural ceramics for various applications, exhibits excellent mechanical strength and superior high temperature properties.

1. Introduction

At present, due to the development of waste-free and resource-saving production methods, mechanical activation (MA) remains attractive to researchers. MA significantly expands the range of available raw materials suitable for the production of important compounds, such as nitrides, carbides and oxynitrides [1 - 4]. Mechanical pre-activation (MPA) perfectly supplements the method of synthesis of inorganic materials in the combustion mode. MPA reduces the synthesis temperature, accelerates synthesis and increases the homogeneity of initial components, improving the quality of final products [5 - 7].

During mechanical activation, reaction mixture components are intensively ground, mixed, and interpenetrate at the micro-scale level, destructing oxide films [6, 8, 9]. An increase in the reactivity of powders during grinding is achieved by two simultaneous processes: an increase in the specific surface of powder, which leads to an increase in the number of uncompensated bonds and to the growth of the contact area between particles. Some amount of energy imparted to the material during mechanical activation is accumulated by the system and consumed to create defects in the crystal structure. Such defects reduce the stability of bonds between atoms and ions and may lead to amorphization of a substance. As a result, the kinetics of combustion reaction changes, which is associated with easier initiation of combustion and its stability.

Self-propagation high-temperature synthesis (SHS) method was developed as a highly-efficient route for the preparation of β-SiAlON. It is promising due to lots of advantages including high rate production, low cost, energy efficiency and simple equipment [10, 11].

In this work, the effect of mechanical pre-activation on the nitriding of aluminum ferrosilicon in the combustion mode was studied. As it was shown earlier [12], aluminum ferrosilicon has a positive effect on the combustion process, since iron contained in the substance acts as a catalyst, and aluminum and silicon are nitride-forming elements. An important product for aluminum ferrosilicon nitriding is β-SiAlON that has high thermal stability up to 1800 °C, as well as high corrosion resistance, high hardness and wear resistance. The outstanding performance properties of β-SiAlON make it possible to consider this material to be prospective in many applications [13 - 15].

2. Materials and procedures

Aluminum ferrosilicon (FS55A20 grade) was used in the study. Chemical analysis showed that the alloy contained: silicon (57.1%), aluminum (18.3%), and iron (the rest). According to X-ray diffraction (XRD), initial aluminum ferrosilicon was a multi-phase material consisting of silicon and high-temperature leboite (FeSi2). The phase composition was determined with a Shimadzu XRD6000 diffractometer (Japan). Before conducting SHS, initial powders were dried in a vacuum oven at a temperature of 150–200 °C to remove moisture and volatile impurities. SHS was carried out in the constant pressure setup.

The setup is a 3-liter thick-walled vessel equipped with inlet and outlet valves, a pressure gauge, an igniting device, as well as observation windows. The prepared reaction mixture was poured into the gas-permeable, cylindrical tubes with a diameter from 20 to 60 mm and burned in a constant pressure setup with a pressure from 10 to 60 MPa. The samples were ignited with the igniting mixture using a tungsten coil through which electric current was passed. The relative density of the samples was ≈ 0.4 g/m^3.

The igniting mixture initiated a chemical reaction with a large heat release. The released heat initiated chemical reactions in the next layer of the sample, resulting in a combustion wave. After the passage of the combustion wave, the sample was kept in the setup until complete cooling for 30 minutes for re-nitriding, and then it was removed for further studies.

The total content of nitrogen and oxygen was determined using a LECO - ONH836 analyzer.
Mechanical activation and grinding of a powder with a particle size of less than 100 μm were conducted in an AGO-3 planetary mill under the argon atmosphere. The volume of the steel drum was 2000 cm^3; the radial acceleration was 60 g, the diameter of the hardened steel balls was 0.5 cm. The ball to powder weight ratio was 10:1.

The time of mechanical activation was varied for two cases. In the first case, mechanical activation was conducted for 5 minutes, i.e. every 5 minutes the mill was stopped and the drums were cooled. In the second case, the time of mechanical activation was 1 minute, i.e. after every minute the mill was stopped and the drums were cooled.

The specific surface of the samples was determined with a SORBI-M instrument, comparing the volumes of the gas-adsorbate sorbed by the test sample and a standard sample with a known specific surface. The specific surface was measured by the 4-point BET method.The particle size distribution was measured using a Fritsch Analysette 22 MicroTec plus Laser Particle Sizer.

3. Results and discussion

At present, mechanical activation is one of the methods to correct the SHS conditions by changing the reactivity of fresh ground solids. As a rule, the reagents prepared by mechanical activation expand the limits of combustion, change the thermal parameters of the front, and increase the rate of SHS.

In the work, mechanical activation and grinding of a powder with a particle size of less than 100 μm were conducted in the AGO-3 planetary mill for 1, 5, and 10 minutes. One of the most important characteristics affecting the combustion of a ferroalloy is the size of powder particles and a specific surface area. Table 1 provides the particle size distribution after mechanical activation. It can be seen that initial aluminum ferrosilicon is characterized by the distribution curves with a broad peak, which indicates the polydispersity of the system. The particle size distribution curves after mechanical activation have two pronounced peaks. Such a distribution is considered to be bimodal. At the same time, increasing the activation time, the bimodality becomes more pronounced.

Table 1. The size distribution of aluminum ferrosilicon particles at different times of mechanical

activation

Without m/a		1 min		5 min		10 min	
% volume	< µm	% volume	< µm	% volume	< µm	% volume	< µm
10	2.2	10	1.2	10	1.2	10	1.1
50	11.8	50	6.7	50	6.5	50	4.9
90	38.0	90	19.2	90	22.8	90	17.8
100	100.0	100	45.0	100	75.0	100	75.0

An increase in the activation time of aluminum ferrosilicon powder leads to the increase in the specific surface area (Figure 1). The monotonous increase in the specific surface indicates the accumulation of fine particles. It is worth noting that during the 5 min powder activation the particles becomes larger and after 10 min activation, the particle size decreases again, which suggests the aggregation of particles. At the same time, the aggregation of particles contributes to the formation of interglobular pores that supplement the intraglobular porous structure of individual particles. Therefore, in general, the specific surface area of the sample does not decrease after 5 min mechanical activation, but even increases relative to the sample subjected to 1 min activation. At the same time, the amount of the finest fraction almost does not change.

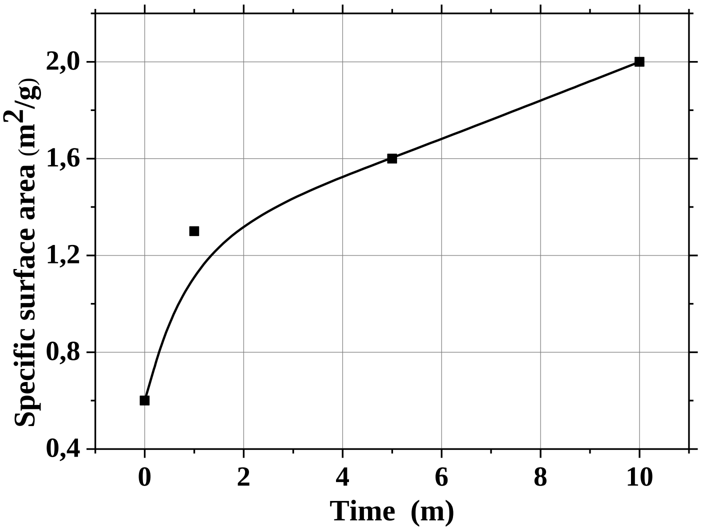

Figure 1. Specific surface area as a function of the mechanical activation time

Combustion of mechanically activated powders occurs in a non-stationary mode, as evidenced by the presence of dark and light zones and cracks in the sample. That is, mechanical activation cannot change the non-stationary combustion mode for the stationary one.

One of the most important parameters affecting the combustion of aluminum ferrosilicon is the nitrogen pressure. Due to mechanical activation, synthesis was initiated at a nitrogen pressure of 1 MPa, while without activation, combustion occurred at 2.5 MPa.

However, an increase in the mechanical activation time leads to the increase in the combustion wave velocities (Figure 2), while the greatest amount of nitrogen is absorbed by the sample activated for 1 minute. This is due to the fact that an increase in the specific surface leads to the increase in the reaction rate. In this case, the heat release rate increases, raising the temperature in the combustion wave and the heating zone. This results in intensive melting of the sample in the heating zone and breaking of gas permeability of the sample. At the same time, nitrogen absorption at the burnout stage (behind the combustion front) decreases. The gas permeability of the samples with an increase in the time of mechanical activation can also be related to an increase in the bimodal particle size distribution, which can provide a denser packing of initial aluminum ferrosilicon particles. In case of filtration supply of nitrogen to the reaction zone, a high density of the sample is undesirable. In general, despite the fact that with an increase in the time of mechanical activation, the content of nitrogen absorbed by the sample decreases, it is still significantly higher compared to the samples without mechanical activation.

During filtration combustion, the diameter of the sample has a great effect on the nitriding process and the composition of products.

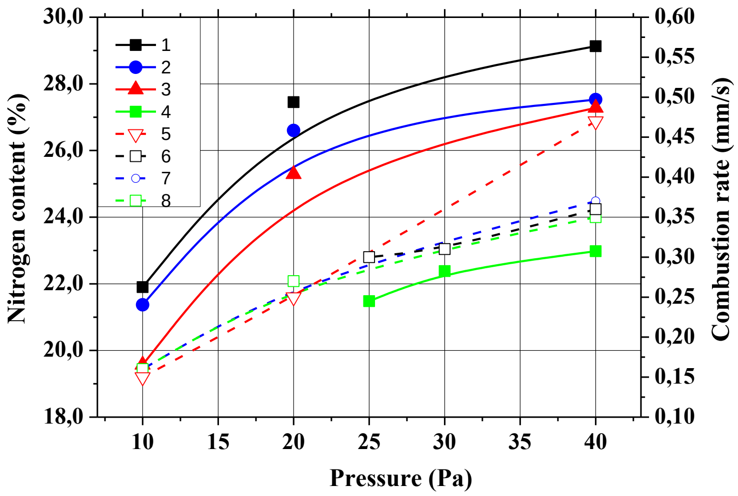

Figure 2. Content of nitrogen in SHS products (1, 2, 3, 4) and combustion rate (5, 6, 7, 8) as a function of pressure and mechanical activation time (MA) of initial aluminum ferrosilicon: 1, 6 - 1 min MA; 2, 7 - 5 min MA; 3, 5 - 10 min MA; 4, 8 - without MA.

Combustion of mechanically activated aluminum ferrosilicon differs from the combustion of initial powder. In particular, mechanical activation expands the combustion parameters and initiates a reaction at smaller diameters. According to experimental data, the combustion of the powders subjected to MA is initiated with a minimum sample diameter (20 mm), while the combustion of the powders without preliminary MA is conducted only if the sample diameter is more than 30 mm.

Studies have shown that increasing the diameter leads to the decrease in the combustion rate (Figure 3), while the combustion rate of activated powders is slightly higher, which is associated with a smaller particle size of initial aluminum ferrosilicon.

Slowing down the process with increasing the sample diameter for both activated and non-activated powders is likely to be related with the increase in the filtration of reacting nitrogen.

An increase in diameter leads to the significant increase in the amount of nitrogen absorbed in samples. As shown in Figure 3, the highest nitrogen absorption is achieved when the powder is subjected to 1 min activation. The sample subjected to 1 min activation burns more slowly than the samples subjected to 5- and 10-min activation. A lower combustion rate increases the residence time of reagents in the high-temperature reaction zone, which ensures a higher degree of nitriding of products.

The X-ray diffraction patterns show that β-$Si_3Al_3O_3N_5$ is formed as the main phase during the nitriding of activated powders, while a mixture of β-Si_3N_4/β-$Si_3Al_3O_3N_5$ phases is formed during the nitriding of non-activated powders. Probably, the combustion of thin mechanically activated powders provides more favorable conditions for the formation of solid solutions based on Si_3N_4, i.e., β β-$Si_3Al_3O_3N_5$.

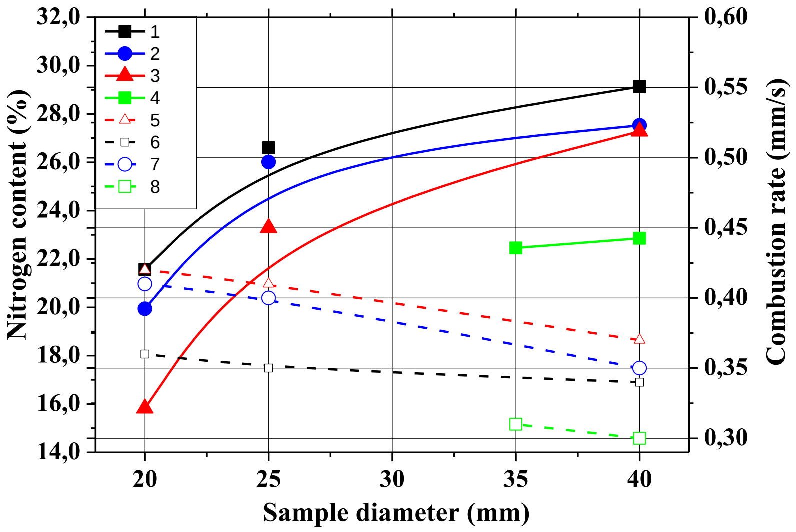

Figure 3. Content of nitrogen in SHS products (1,2,3,4) and combustion rate (5,6,7,8) as a function of the diameter and time of mechanical activation of initial aluminum ferrosilicon: 1, 6 - 1 min MA; 2, 7 - 5 min MA; 3, 5 - 10 min MA; 4, 8 - without MA.

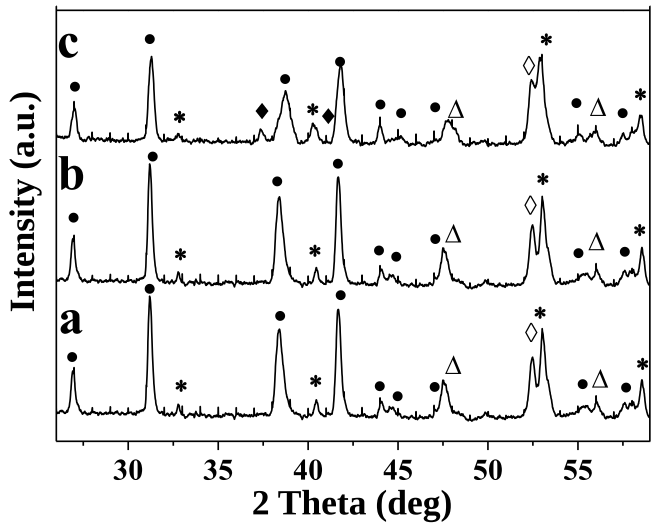

Figure 4. Phase composition of the products obtained during the combustion of aluminum ferrosilicon in nitrogen at different activation times: (a) 1 min., (b) 5 min., (c) 10 min.
● – β-$Si_3Al_3O_3N_5$, * – FeSi, ♦ – SiAlON, Δ – $FeSi_2$, ◊ – Fe.

At the same time, a significant amount of iron silicides (FeSi and $FeSi_2$) is detected in nitrided samples, which indicates that the process of nitride formation is incomplete. Analysis of X-ray diffraction patterns showed that with an increase in the activation time of the initial alloy to 10 minutes, the main reflex β-$Si_3Al_3O_3N_5$ decreased. An additional phase of sialon, SiAlON, appears. This phase is referred to the 15R polytype and formed on the basis of AlN.

Thus, the study conducted to investigate the effect of mechanical activation on the combustion of aluminum ferrosilicon showed that:

- Mechanical activation of initial powders initiates SHS reaction at lower pressures and diameters, i.e. expands the parameters of combustion of aluminum ferrosilicon in nitrogen.

- Mechanically activated powders used in SHS processes allows a product with a higher nitrogen content to be obtained.
- Nitriding of mechanically activated powders can be used to obtain a reaction product consisting mainly of β-$Si_3Al_3O_3N_5$.
- The presence of initial components in the reaction products, as well as intermediate products of dissociation indicates an incomplete conversion.

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Notification

MPA – Mechanical pre-activation

SHS - Self-propagation high-temperature synthesis

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