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Effect of aluminium oxide and ash microspheres on nitriding of aluminium ferrosilicon in the combustion mode

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Abstract. A composite ceramic β-sialon-based material is obtained by the SHS method using aluminium ferrosilicon as an initial material. The effect of the addition of aluminium oxide (α-Al₂O₃) and ash microspheres on the synthesis of sialon is studied. The iron-containing sialon-based composite is shown to exhibit a high catalytic activity in the presence of H₂O₂, H₂C₂O₄ during degradation of dyes and phenol under UV radiation.

1. Introduction

At present, nitrides are one of the most widely used materials due to their high strength, thermal and chemical resistance to many corrosion media, and therefore they are promising for use in various areas of modern engineering [1]. Of particular interest are β-sialons which are solid solutions with variable composition (Si₆₋₇AlₓOₓN₈₋₇ₓ) formed on the basis of β-Si₃N₄ by substitution of Si → Al and N → O (x is the number of substituted silicon and nitrogen atoms in the formula of silicon nitride, changes from 0 to 4.2). These compounds are resistant to high temperatures (1500-1800°C), have high corrosion, heat and wear resistance, high hardness and strength [2, 3] and are currently considered to be commercially and technologically promising materials. As a rule, expensive highly dispersed powders are used for the production of nitrides and nitride-based materials. So, there is a problem concerning the search of cheap initial materials for the production of nitrides and nitride-containing composites. In this regard, the use of industrial ferroalloys, as cheaper reagents, can significantly reduce the cost of nitrides and nitride-based materials. At the present time, the synthesis of sialons is combined with the process of hot pressing of preliminary obtained powder mixtures Si₃N₄, AlN and Al₂O₃, which leads to the high cost of ceramic materials. In our opinion, one of the most cost-efficient methods for obtaining nitrides is the self-propagating high-temperature synthesis (SHS) method, since synthesis is conducted almost without energy costs. Advantages of the SHS method are the rapid and one-stage synthesis process. The works [4, 5] use simple industrial ferroalloys containing a single nitride-forming element for the obtaining of nitrides by the SHS method. Composite ferroalloys containing several nitride-forming elements are particularly attractive in view of the scientific and applied aspect. Most of the nitrides of metals and nonmetals are semiconductor compounds which can provide the obtained materials with optical activity.

The use of multicomponent ferroalloys is of interest for the synthesis of composite metal-ceramic materials to be used use as photocatalysts of degradation of soluble organic substances. A number of works [6, 7] already reported the high photocatalytic activity of composites based on boron and silicon nitrides obtained by the SHS method during degradation of phenolic compounds and formaldehyde.
The direction aimed to study the abilities of composite ferroalloys is a promising continuation of the works carried out by the scientists at the Department for Structural Macrokinetics of Tomsk Scientific Center of SB RAS.

2. Materials and procedures

The objects of the study were the modified silicon nitride-based composites obtained by the high-temperature self-propagating synthesis (SHS) method at the Department for Structural Macrokinetics of Tomsk Scientific Center of SB RAS. The phase composition of the materials was studied by X-ray diffraction (XRD) on a diffractometer (XRD6000, Japan, Shimadzu). X-ray diffraction analysis data were processed using the POWDER CELL 2.5 full-profile analysis program and the Scherrer equation. Aluminium ferrosilicon (FS56515) was used as initial material. According to the data of X-ray diffraction analysis, initial aluminium ferrosilicon was a multiphase material consisting of silicon and high-temperature leboite (FeSi$_2$). X-ray microanalysis of initial aluminium ferrosilicon showed that aluminum was mainly in the composition of solid FeSi$_2$-based solution, forming two phases with a different ratio of silicon and aluminum: FeSi$_{2.2}$Al$_{0.4}$ and FeSi$_{1.6}$Al$_{2.2}$. There were the impurity phases: Al$_2$O$_3$ and Al$_{0.5}$Fe$_{0.5}$. The chemical analysis showed that the alloy contained silicon in the amount of 60.1%, aluminum – 13.2%, and iron – 26.7%. The additives used were ash microspheres which are the products of burning fuels at thermal power stations and have the form of finely dispersed hollow microspheres with a basic composition: SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$. Aluminium oxide had α-Al$_2$O$_3$ modification.

The total content of nitrogen and oxygen was determined using a LECO-ONH836 (USA) analyzer. The method is based on the melting of a sample in a high-purity graphite crucible at a temperature above 3000 °C under helium. Oxygen in the sample reacts with carbon from the crucible to form carbon monoxide, and nitrogen is released in the form of molecular nitrogen. Oxygen is detected in the phases of CO and CO$_2$ using an infrared detector. Nitrogen is detected using a detector of thermal conductivity. The maximum combustion sample temperature achieved during the nitriding of the alloy was measured with tungsten-rhenium thermocouples BP5/BP20 200 μm in diameter. The uncovered part of the thermocouple, which was inside the sample, was covered with a thin layer of boron nitride, leaving only the junction uncovered.

The thermocouple was embedded into the sample at a depth of 10-15 mm. The thermocouple readings through the analog-to-digital converter LA-20 USB were transferred to a personal computer and processed using graphic editors. The combustion process was recorded with a video camera. The velocity of the combustion front propagation was measured with a stopwatch.

Polydispersed powder with a particle size of less than 100 μm was used for the experiments. Nitriding of the alloy by the SHS method was carried out in a constant pressure unit. Before conducting the SHS process, the alloy was ground to obtain required dispersity and dried to remove moisture and volatile impurities. The mixture was placed into cylindrical tubes made of metal mesh. The samples were burned in the constant pressure unit at nitrogen pressure of 6 MPa by the procedure in [8]. The samples were ignited from the powder ignition mixture with a tungsten spiral, through which electric current was supplied. Under the spiral there was a zone of chemical reactions with high heat release. The released heat initiated chemical reactions in the next layer of the sample, which lead to the formation of a combustion wave that was observed through an observation window of the unit as a glowing zone. After passing through the combustion front, the sample was kept in the unit under nitrogen until it was completely cooled. Then the pressure was dropped, and the SHS product was used for the further study.

3. Results and discussion

3.1. Combustion of aluminium ferrosilicon in the presence of ash microspheres

Experiments have shown that the combustion of aluminium ferrosilicon in nitrogen occurs in the nonstationary mode. The combustion wave propagates as follows. After the initiation of reaction a
bright flash is observed and a wide combustion front occurs. Then a crack is formed, which is probably caused by shrinkage of the alloy due to its melting. When nitriding aluminium ferrosilicon, the combustion products contain the $\beta$-sialon phase ($\beta$-$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$) as well as silicon nitride. In addition, the presence of iron silicides in the combustion products indicates an incomplete conversion of the initial reagents. Ash microspheres are the products of burning fuels at thermal power stations and have the form of spherical granules with a smooth outer surface 20-500 microns in size and a bulk density of 380-420 kg/m$^3$. The use of aluminosilicate hollow microspheres as an additive to aluminium ferrosilicon to obtain $\beta$-$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ is caused by two reasons:

1. Since the microspheres are hollow and have a high bulk density, it is possible to improve the filtration characteristics of the sample, which in turn will lead to an increase in the degree of nitriding of synthesis products.
2. Microspheres contain $\text{SiO}_2$, $\text{Al}_2\text{O}_3$ that are the main initial materials for the obtaining of sialons.

In the work [9] $\beta$-$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ was obtained from ash wastes by the method of carbothermic reduction under nitrogen. However, the product obtained was contaminated with carbides, oxynitride compounds of aluminum, as well as with initial components. The nitriding of aluminium ferrosilicon in the presence of ash microspheres in an amount of more than 10 wt.% changes the nonstationary combustion mode to the stationary one. Figure 1 shows the images of the combustion products (aluminium ferrosilicon) in nitrogen in the presence of 15 wt.% additive of aluminosilicate microspheres. It can be seen that the combustion product is a sintered porous material homogeneous throughout the volume. The studies have shown that the pore size of the sample is usually determined by the particle size of ash microspheres. Thus, the porosity of the material obtained can be controlled if the certain fraction of ash microspheres is separated and added to the initial material. In the case when the amount of additives added to the initial material was more than 25 wt.%, the combustion of aluminium ferrosilicon was not initiated.

![Figure 1](image1.png)

**Figure 1.** Images of the combustion product (aluminium ferrosilicon) in nitrogen (a) and its cross section (b) in the presence of 15 wt.% additive of aluminosilicate spheres.

Figure 2 shows the degree of nitriding and the velocity of the combustion wave propagation as a function of the amount of the additive. It is seen that with the increase in the amount of the additive, the velocity of the combustion wave propagation decreases. The degree of nitriding reaches the maximum value in the presence of 15 wt.% additive and then decreases. Apparently, the addition of ash microspheres to the initial material has a double effect. On the one hand, an increase in the inert
additive reduces the combustion temperature, as evidenced by the thermograms of the combustion process (figure 3). The decrease in the combustion temperature is due to the fact that during nitriding the total mass of the sample increases, and the inert additive does not contribute to the heat release. On the other hand, the additive influences on the filtration of nitrogen in the initial mixture. The increase in the amount of the additive decelerates the sintering of material, which increases the gas permeability of the sample.

If the first factor reduces the combustion temperature and, correspondingly, reduces the reaction rate and the amount of nitrogen adsorbed, the second factor contributes to the increase in the absorption of nitrogen behind the combustion front where volume aftercombustion takes place. The fact that the nitriding process is continued is evidenced by the long time of the sample glow after the passage of the combustion front, and also by the increased cooling time on the temperature profile (figure 3).

In general, ash microspheres can be used as additives to change the surface combustion mode to the layer-to-layer combustion mode in order to obtain a sample with a homogeneous macrostructure, as well as to obtain a sintered porous material. When 15 wt.% additives are added to the initial ferroalloy, the predominant phase in the combustion products is $\beta$-$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$.

![Figure 2. Degree of nitriding (1) and the velocity of the combustion wave propagation (2) as a function of the amount of addition of ash microspheres.](image_url)

When hollow microspheres are added to aluminium ferrosilicon, the phase composition of the combustion products depends on the amount of the additive. When ferroalloy burns in nitrogen without additives, the amount of $\beta$-$\text{Si}_3\text{N}_4$ in the combustion products predominates over the amount of $\beta$-$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$. The same dependence is maintained when 5 wt.% ash microspheres are added to the initial material. In addition, there is a sufficient amount of initial components in the combustion products. With the increase in the amount of the additive, the amount of the $\beta$-$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ phase gradually increases, and in the presence of 10 wt.% additive the amount of sialon and silicon nitride phases becomes almost the same.

Reflections of the initial components and products of step dissociation of iron silicide are detected in the reaction products. The highest absorption of nitrogen is observed when 15 wt.% additives are added to the initial material. In this case, the reflections of $\beta$-$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ significantly predominate.
over the reflections of $\beta$-$\text{Si}_3\text{N}_4$. Combustion products do not contain initial reagents. The appearance of Fe$_3$Si$_3$ phase (product of step dissociation of FeSi$_2$) in the composition of the synthesis product and a significantly increased reflection of $\alpha$-iron indicate a deeper reaction. The increase in the amount of additives leads to a significant decrease in the synthesis temperature, which results in the decrease in the degree of nitriding of the products. At the same time, a significant amount of unreacted initial components (FeSi$_2$, Si) is contained in the combustion products.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Thermograms of the combustion of aluminium ferrosilicon in nitrogen and in the presence of ash microspheres: (a) without additives, (b) 25 wt.%, (c) 15 wt.%.}
\end{figure}

3.2. Combustion of aluminium ferrosilicon in the presence of aluminium oxide

To achieve the maximum possible degree of nitriding of the synthesis products and obtain $\beta$-sialon with a $\beta$-$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ composition, the additives of $\alpha$-$\text{Al}_2\text{O}_3$ in the amount of 5-22 wt.% were additionally added to the initial material. When the amount of Al$_2$O$_3$ was more than 22 wt.%, the combustion of aluminium ferrosilicon was not initiated. The addition of aluminium oxide in the amount of more than 5 wt.% changes the nonstationary combustion mode to the stationary one. Figure 4 shows the nitrogen content and the combustion rate of aluminium ferrosilicon as a function of the amount of the aluminium oxide additive.

It can be seen from figure 4 that with the increase in the amount of additive, the amount of nitrogen absorbed changes insignificantly, and the combustion rate gradually decreases. A gradual decrease in the combustion rate is associated with an increase in the amount of the $\alpha$-Al$_2$O$_3$ inert additive in the initial material, which leads to a gradual decrease in the maximum reaction temperature (figure 5). A detailed study of the diffraction profile obtained for the combustion products of aluminium ferrosilicon in the presence of Al$_2$O$_3$ additives showed that all diffraction maxima shifted toward smaller angles (20).

Interplanar distances were calculated for the different contents of aluminum oxide in the initial material. The values obtained were compared to the reference values of $\beta$-sialon with a composition of Si$_3$Al$_3$O$_5$N$_5$ ([36-1333] JCPDS data file). It was found that with the increase in the amount of the aluminum oxide additive, the parameters of the crystal lattice were close to the reference values of $\beta$-Si$_3$Al$_3$O$_5$N$_5$ and reach the maximum match for 22 wt% Al$_2$O$_3$. In this case, a two-phase combustion product consisting of $\beta$-Si$_3$Al$_3$O$_5$N$_5$ and $\alpha$-Fe was formed. To obtain pure sialon, it is sufficient to treat the combustion product with a weak solution of hydrochloric acid.
Figure 4. Nitrogen content in products (1) and combustion rate (2) as a function of the amount of $\alpha$–$\text{Al}_2\text{O}_3$ additive (nitrogen pressure is 4 MPa).

Figure 5. Thermograms of the combustion of aluminium ferrosilicon in nitrogen in the presence of $\alpha$-$\text{Al}_2\text{O}_3$: (a) 22 wt.%, (b) 10 wt.%, (c) without additives.

Since the obtained metal-ceramic composite, along with the main phase of $\beta$-sialon, also contains a metallic iron phase ($\alpha$-Fe), it is of interest to evaluate its catalytic activity during the degradation of dyes (methyl orange (MO), methylene blue (MB), bromothymol blue (BTB)) and phenol in different photocatalytic systems. Thus, the partial dissolution of $\alpha$-Fe phase in the presence of activating reagents ($\text{H}_2\text{O}_2$, $\text{H}_2\text{C}_2\text{O}_4$) leads to the formation of photo-catalytic systems (photo-Fenton, ferrioxalate) generating super oxidizers (hydroxyl radicals) that can deeply oxidize soluble organic substances to
form ecologically safe products: water and carbon dioxide. In the absence of activating reagents, under UV radiation, the degradation of soluble organic substances can be conducted with the participation of ceramic matrix, since sialon refers to wide-gap semiconductors capable of absorbing UV radiation and simplifying the electron transfer processes. Table 1 provides the evaluation of the photocatalytic activity of sialon.

**Table 1.** Degradation (%) of soluble organic substances in different photocatalytic systems 
($C_{MO}=5 \text{ mg/L}, C_{MB}=S_{BTB}=10 \text{ mg/L}, C_{Ph}=0.05 \text{ mg/L}, m_{kt}=100 \text{ mg}, V_{s-n}=10 \text{ ml}, \tau_{(UV)}=10 \text{ min}$).

| Dye      | Absorption | UV  | UV/H$_2$O$_2$ | UV/H$_2$C$_2$O$_4$ | UV/H$_2$O$_2$/H$_2$C$_2$O$_4$ |
|----------|------------|-----|--------------|--------------------|-------------------------------|
| MO       | 8          | 7   | 13           | 89                 | 100                           |
| MB       | 22         | 35  | 27           | 95                 | 100                           |
| BTB      | 28         | 36  | 39           | 60                 | 98                            |
| Pheno    | 12         | 24  | 56           | 48                 | 97                            |

It can be seen that the composite obtained exhibits high activity during the degradation of different soluble organic substances and can be a promising material for purification of sewage from organic pollutants. UV radiation and the addition of activating reagents lead to combined homogeneous and heterogeneous catalysis. It was shown that nearly 100% degradation of the investigated soluble organic substances was observed in a peroxide-ferrioxalate system (UV/H$_2$O$_2$/H$_2$C$_2$O$_4$) in the presence of sialon.

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