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Nitriding of ferrochromium-aluminum during combustion and evaluation of the photocatalytic activity of obtained composites

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Abstract. The paper represents the possibility of nitriding of ferroalloy (ferrochromium-aluminum) by the method of self-propagating high-temperature synthesis. The main ferroalloy nitriding characteristics, such as the nitriding degree and the combustion rate are determined versus the sample diameter, nitrogen pressure and dispersity of the initial powder. Combustion of the alloy is found to take place in a layer-by-layer mode. The photocatalytic activity of the obtained ferrum-containing nitride composites during the degradation of soluble organic matters (dyes, phenol, diclofenac sodium) is evaluated. High efficiency of the obtained materials is observed by combining heterogeneous and homogeneous catalysis.

Introduction

Combustion of different metal powders under the nitrogen atmosphere was presented for the first time in the works conducted by A.G. Merzhanov [1]. The method is based on exothermic reactions proceeding in the combustion mode with the formation of valuable compounds and materials after passing the front of combustion wave. The combustion wave propagates due to the heat release of the chemical reaction in the initial layer and the transfer of heat to initiate an exothermic chemical reaction in the subsequent layer of the initial mixture [2]. The method of self-propagating high-temperature synthesis (SHS) is promising due to its significant advantages: low energy consumption, environmental friendliness, small-sized equipment, a large number of available raw materials, high-speed production of products, etc. [3]. As a rule, expensive powders are used as initial materials for SHS, which significantly increase the cost of final products [4]. The cost of the products obtained is significantly reduced when raw materials that are not subjected to deep cleaning are used as initial reagents, in particular, ferroalloys. The works [5, 6] demonstrate the use of ferroalloys for SHS and show that the properties of the combustion product are comparable with the properties of the products obtained from pure precursors. In our opinion, the most promising materials for SHS conducted in the mode of filtration combustion under the nitrogen atmosphere are ferroalloys, since these alloys can contain several nitride-forming elements and are interesting both from a theoretical and practical view. Ferrum contained in alloys catalyzes the nitriding of nitride-forming elements. The decomposition of ferroalloys allows nitrides of elements to be obtained in one stage. In this regard, ferroalloys are promising both in scientific and applied aspects, but at the same time they are complicated reagents for the synthesis of nitride-containing composites and nitrides. To control synthesis and solve the main



task of SHS - obtaining the product with a required phase composition and a microstructure determining its properties, it is necessary to determine the characteristics of the nitriding process using ferroalloys as reagents. Earlier it was found that ferrum-containing metal-ceramic composites based on boron nitride, sialon, silicon and titanium [7] exhibit a high catalytic activity during oxidative degradation of soluble organic matters in the presence of activating reagents (H_2O_2 , $\text{H}_2\text{C}_2\text{O}_4$, EDTA) and UV radiation, forming photoactive systems, such as Photo-Fenton, ferrioxalate and ferriccomplexonate systems ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$, $\text{Fe}(\text{C}_2\text{O}_4)^{3-}_3/\text{UV}$, $\text{Fe}/\text{EDTA}/\text{UV}$) [8, 9]. Catalytic processes occur due to the high oxidative ability of OH-radicals [10] which are formed in the presence of composites and activating reagents. The photocatalytic activity of ferrum-containing metal-ceramic composites is related not only to the participation of ferrum in the formation of OH-radicals, but also to the presence of semiconductor phases in the ceramic matrix, which provide optical properties.

This paper presents studying the characteristics of combustion of ferrochromium-aluminum in nitrogen and evaluation of the catalytic activity of the product obtained.

Materials and methods

A ferroalloy (ferrochromium-aluminum) with a content of 8.5% aluminum, 30% ferrum, 61.2% chromium and 0.3% impurities was chosen to study the characteristics of combustion. The phase composition was determined using a Shimadzu XRD6000 diffractometer (Japan). According to X-ray phase analysis, ferrochromium-aluminum contains the phases as follows: AlFe, Cr, AlFeCr₂. Before synthesis, ferrochromium-aluminum was dried in a CHVS-40/3.5 vacuum oven (Russia) for 3 hours at a temperature of 150°C to remove water and volatile impurity compounds.

Ferrochromium-aluminum was placed on a cylindrical metal mesh with a diameter from 5 to 60 mm in a constant pressure unit on a non-conductive stand and burned at a pressure from 1 to 8 MPa. The combustion reaction was initiated by electric pulse supplied from the transformer through a tungsten coil. After the initiation of chemical reaction in initial ferrochrome with nitrogen, the movement of the combustion wave front was observed. After complete passage of the combustion wave, the sample was kept in the unit under the nitrogen atmosphere for 30 minutes until complete cooling, and then pressure was released and the obtained composite was studied.

The total content of nitrogen in the products was determined using a LEKO-ONH836 (USA) device.

The photocatalytic activity of nitrided composites was investigated by the following method: a sample of catalyst in the amount of 100 mg was placed in a quartz glass, and an organic pollutant solution (phenol, methylene blue, diclofenac sodium) in the amount of 10 ml and a few drops of activating reagent (H_2O_2 , $\text{H}_2\text{C}_2\text{O}_4$) were added. The quartz glass with the reaction solution was covered and placed on a magnetic stirrer in front of the radiation source for a certain time. Analytical control of the concentration of pollutants was performed by the spectrophotometric method: methylene blue (MB) at $\lambda \sim 660$ nm, eosin at $\lambda \sim 515$ nm, diclofenac sodium at $\lambda \sim 275$ nm, phenol with 4-aminoantipyrine at $\lambda \sim 510$ nm. The degradation degree of the pollutant (R) was calculated by the formula:

$$R, \% = \frac{(c_{init} - c_{fin})}{c_{init}} 100,$$

where C_{init} is the initial concentration of SOM, and C_{fin} is the final concentration of SOM.

Results and discussion

In contrast to ferrochromium-aluminum, nitriding of ferrochrome by the SHS method is possible if preheating of an alloy to 300 C is conducted. The content of chromium in the initial mixture should exceed 75%. Studies have shown that the combustion of ferrochromium-aluminum occurs in the layer-by-layer mode. In this case, the initial mixture does not require preheating, and the content of chromium is 61%. According to X-ray phase analysis, the product obtained by nitriding of

ferrochromium-aluminum is multiphase and contains the phases as follows: CrN, α -Fe, $(\text{Cr,Fe})_2\text{N}_{1-x}$, Cr_2N . Aluminum nitride, as a separate phase, is not detected, however, according to X-ray microanalysis, this phase is contained in chromium nitride. This is confirmed by the broadening of CrN reflexes presented in the X-ray pattern (figure 1).

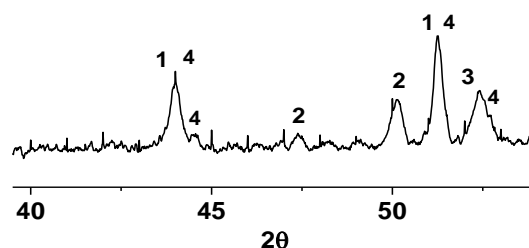
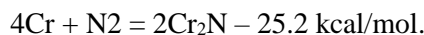


Figure 1. X-ray pattern of nitrated ferrochromium-aluminum
(1 – CrN, 2 – $(\text{Cr,Fe})_2\text{N}_{1-x}$, 3 – α -Fe, 4- AlN).

As a rule, the reaction of chromium nitriding consists of two stages:

The first stage is the Cr_2N reaction:



The second stage is the CrN reaction:



The CrN system is characterized by a low calculated adiabatic combustion temperature (2063 °C). The presence of $(\text{Cr,Fe})_2\text{N}_{1-x}$ phase (Cr_2N phase, where the chromium atoms are partially replaced by ferrum in the products indicates that the nitriding process is incomplete, since not all Cr_2N turned into CrN.

For filtration combustion, one of the important factors affecting this process is nitrogen pressure. The value of initial pressure has a significant effect on the filtration characteristics and the nitriding degree of synthesized products. Usually the maximum pressure used in SHS processes is 10 MPa. Experiments have shown that the increase in pressure leads to a monotonic increase in the amount of nitrogen absorbed and in the combustion rate (figure 2). Then these values reach a maximum that corresponds to the nitriding degree of chromium. The study of the nitriding degree, combustion rate and phase composition as a function of nitrogen pressure showed that the combustion of the samples began at a minimum pressure of 1.5 MPa.

The phase composition of the products of ferrochromium combustion in nitrogen depends on the pressure of nitrogen. When the nitrogen pressure is above 8 MPa the main phase is CrN, at a pressure of 2-8 MPa a mixture of CrN and $(\text{Cr,Fe})_2\text{N}_{1-x}$ phases is present, and at $P < 2$ MPa the predominant phase is $(\text{Cr,Fe})_2\text{N}_{1-x}$.

The study of the nitriding degree, combustion rate and phase composition of the obtained composites versus the diameter of samples showed that the combustion reaction was initiated in a sample with a minimum diameter of 15 mm. The increase in the sample diameter leads to the slight decrease in the amount of nitrogen absorbed, and a relatively constant combustion rate is observed. These results are associated with two parallel factors: difficulties with filtration of gas towards the reaction zone and a decrease in heat loss in the reactor volume. In this case, the phase composition remains almost unchanged.

The study of the of nitriding degree, combustion rate and phase composition versus the dispersity of the initial powders showed that the samples with a particle size of more than 100 μm and up to 100 μm (40-63, 63-100) in the absence of a fine fraction did not burned. The effect of dispersity on the amount of nitrogen absorbed and the rate of combustion is presented in Figure 4. A decrease in the particle size of the initial powder leads to a significant increase in the amount of nitrogen absorbed and

the rate of combustion. This is due to the fact that the heat release during the combustion of coarse powders is much lower than for fine powders.

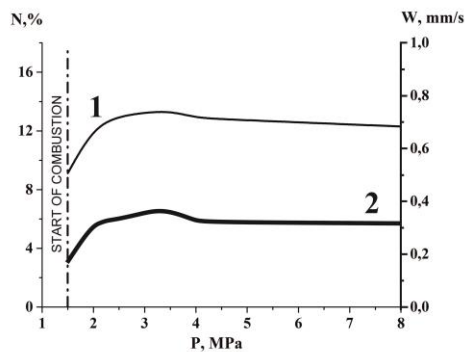


Figure 2. Content of nitrogen (1) and combustion rate (2) as a function of nitrogen pressure.

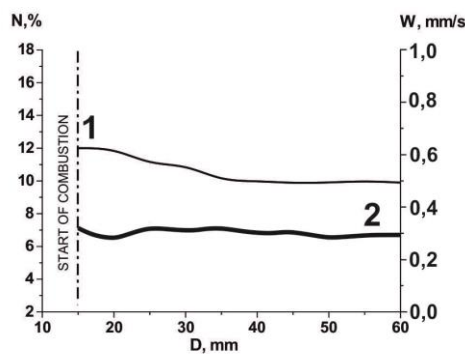


Figure 3. Content of nitrogen (1) and combustion rate (2) as a function of the sample diameter.

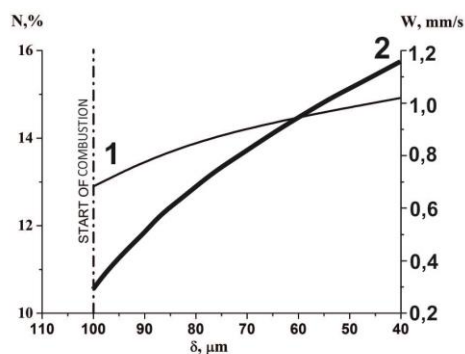


Figure 4. Content of nitrogen (1) and combustion rate (2) as a function of the particle size.

The obtained metal-ceramic composite contains a phase of CrN chromium nitride that is a narrow-bandgap semiconductor [11] and can participate in heterogeneous photocatalysis. At the same time, the composite contains the phase of metallic ferrum (α -Fe) the partial dissolving of which in the presence of H_2O_2 or $\text{H}_2\text{C}_2\text{O}_4$ forms the homogeneous photocatalytic Photo-Fenton and ferrioxalate systems generating a superoxidant - hydroxyl radicals. The catalytic activity of the synthesized sample during oxidative destruction of some organic pollutants (phenol, methylene blue, eosin, diclofenac sodium) was evaluated for different photocatalytic systems.

To identify the role of ceramic matrix in the photocatalytic process, the destruction of organic pollutants exposed to UV radiation was investigated in the absence and presence of a composite but without the addition of activating reagents. Figure 5 shows the degradation degree of diclofenac sodium as a function of time.

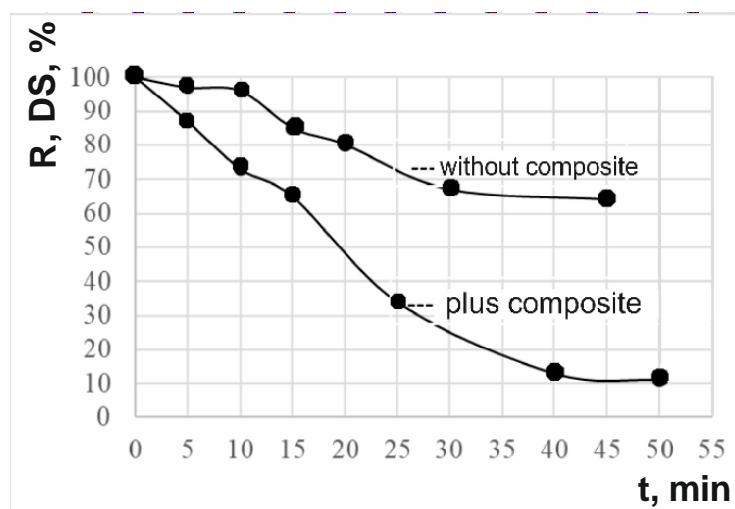


Figure 5. Effect of UV-radiation on the degradation degree of diclofenac sodium (DS) in the absence and presence of an iron-containing composite ($m_{kt} = 100$ mg, $c_{DS} = 25$ mg/l, $v_{sol} = 10$ ml).

It can be seen that the main destruction of organic pollutant occurs within 40 minutes. In the presence of a composite, the degree of degradation is almost 50% greater than the degradation degree of diclofenac sodium in the absence of a catalyst. This indicates the activity of ceramic matrix during the oxidative destruction of SOM.

Table 1 shows the catalytic activity of the synthesized composite in the absence and presence of H_2O_2 and $H_2C_2O_4$ additives during the degradation of the SOM studied. In the absence of activating reagents and presence of UV radiation, degradation of DOM can be conducted with the participation of ceramic matrix, since CrN is a semiconductor capable of absorbing UV energy and facilitating electron transfer processes. In the presence of UV radiation and the addition of activating reagents to the solution, the destruction degree of SOM increases significantly, which may be related to the participation of OH radicals in the catalytic process, which are generated by the photocatalytic ferrioxalate and Photo-Fenton systems formed in solution. Moreover, the efficiency of Photo-Fenton process is higher.

Table 1. Degradation (%) of SOM for different photocatalytic systems ($c_{MB} = 5$ mg/l, $c_{phenol} = 0.5$ mg/l, $c_{DS} = 25$ mg/l, $c_{H_2O_2} = c_{H_2C_2O_4} = 0.002$ M, $m_{kt} = 100$ mg, $V_{sol} = 10$ ml, $\tau_{(UV)} = 15$ min)

SOM	UV	UV/ $H_2C_2O_4$	UV/ H_2O_2
Methylene blue	21	64	97
Eosine	31	69	93
Diclofenac sodium	37	51	100
Phenol	28	48	87

Thus, the obtained composite exhibits a high activity during the degradation of different SOMs and is promising for the purification of wastewater from organic pollutants. The photocatalytic activity of Fe-containing compositions in the presence of activating reagents is related to the combination of homogeneous and heterogeneous catalysis.

The characteristics of the combustion of ferroalloy (ferrochromium-aluminum) were determined for different diameters, nitrogen pressure and dispersity of the initial powder. The main conditions

were found for the initiation of reaction. The photocatalytic activity of the samples obtained during the oxidative destruction of SOM was evaluated.

Acknowledgments

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