Combustion synthesis of metal-ceramic silicon nitride-based composites and their photocatalytic activity

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Abstract. The paper represents the method for obtaining and evaluating the catalytic properties of metal-ceramic composites based on silicon and titanium nitrides. The optimum conditions of the materials synthesis in the combustion mode are determined. The results have shown that the obtained iron-containing composites in the presence of \( \text{H}_2\text{O}_2 \), \( \text{H}_2\text{C}_2\text{O}_4 \), EDTA have a catalytic activity during the degradation of dyes exposed to UV radiation. The addition of TiN to the ceramic matrix is shown to increase the efficiency of photocatalytic generation of hydrogen from carboxylic acids.

1. Introduction

Recently, heterogeneous photocatalysis has been successfully used to remove soluble organic substances (SOS) using the high oxidizing ability of hydroxyl radicals [1-3]. Ozonation and UV radiation contributes to the formation of OH radicals in the presence of oxygen-containing catalysts and reagents. Homogeneous photocatalysis are most widely used for Photo-Fenton and ferrioxalate systems [4, 5]. We have established [6] that iron-containing composites based on boron, silicon and sialon nitrides exhibit a high catalytic activity under UV radiation during the degradation of oxalic acid, phenols, formaldehyde, and dyes. The activity of materials is found to be caused by the presence of metal iron in the composition of their matrix and by the formation of photoactive Photo-Fenton (\( \text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV} \)), ferrioxalate (\( \text{Fe}(\text{C}_2\text{O}_4)_3^{2-}/\text{UV} \)) and ferricomplexonate (\( \text{Fe}/\text{EDTA}/\text{UV} \)) systems in the solution when adding the reagent activators (\( \text{H}_2\text{O}_2 \), \( \text{H}_2\text{C}_2\text{O}_4 \), EDTA). The results also show that the photoactivity of metal-ceramic composites during the degradation of soluble substances depends on the optical properties of the matrix that contains semiconductor compounds.

Silicon nitride and silicon nitride-based materials have a high strength, thermal and chemical resistance to corrosive media, and therefore they are promising for use in various fields of modern engineering [7]. At present, the synthesis of silicon nitride and silicon nitride-based materials is conducted using iron-silicon alloys as initial reagents [8, 9]. Of particular interest is the study of the nitriding of composite alloys containing several nitride-forming elements. One of the promising methods for obtaining nitrides is the method of self-separating high-temperature synthesis (SHS) that is characterized by high productivity and low energy consumption, which is very important for industrial production. The authors have shown that the FSA alloy can be used as an initial material for the obtaining of metal-ceramic silicon nitride-based compositions.
The material obtained contains a sufficient amount of iron to conduct the photocatalytic degradation of soluble organic substances and the addition of semiconductor phases to the ceramic matrix may contribute to deeper degradation of organic pollutants. To improve the photocatalytic activity of silicon nitride-based composites, it was of interest to modify the ceramic matrix by adding semiconductor compounds to its composition, in particular titanium nitride.

2. Materials and methods

The objects of the study were modified silicon nitride-based composites obtained by the 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 using an XRD6000 diffractometer (Shimadzu, Japan). FSA (FS65A15) was used as a green mixture. The data of X-ray diffraction (XRD) showed that the initial FSA was a multiphase material consisting of silicon and high-temperature leboite (FeSi$_2$).

X-ray microanalysis of initial ferrosilicoaluminum shows that aluminum is in the composition of a solid solution based on FeSi$_2$, forming two phases with the different ratio of silicon and aluminum: FeSi$_2$,2Al$_{0.4}$ and FeSi$_1$,6Al$_{2.2}$. The impurity phases are as follows: Al$_2$O$_3$ and Al$_{0.5}$Fe$_{0.5}$. The chemical analysis showed that the alloy contained silicon (60.1%), aluminum (13.2%), and iron (26.7%). Metallic titanium (PTM-1) containing the impurities such as N-0.08, C-0.05, H-0.35, Fe+Ni-0.40, Si-0.10, Cl-0.004 (wt.%) was used as an additive.

X-ray analysis data were processed using the POWDER CELL 2.5 full-profile analysis program and the Scherrer equation. The total content of nitrogen and oxygen was determined using a LECO-ONH836 device (USA). The FSA powder was placed into cylindrical tubes made of metal mesh 40 mm in diameter. The samples were burned in a constant-pressure device at a nitrogen pressure of 6 MPa. The ignition was initiated by the powder ignition mixture with a tungsten spiral, through which electric current was supplied. After passing the combustion front, the sample was kept under nitrogen until it was completely cooled, then the pressure was dropped, and the SHS product was used for the further study.

The photocatalytic activity of the composites during the degradation of soluble organic substances was studied using a technique as follows: a composite with a mass of 200 g was placed in a 100 ml quartz container, which was filled with a dye solution in the amount of 20 ml, and then 2 drops of 0.1 M $\text{H}_2\text{O}_2$ or 0.1 M $\text{H}_2\text{C}_2\text{O}_4$ were added. The container was closed and placed on a magnetic stirrer located in front of the radiation source. A high-pressure mercury lamp (DRL-250) with the most intense line at 254 nm was used as a source of UV radiation.

The content of dyes in reaction systems was controlled by the spectrophotometric method using the SF-56 device (Russia): methylene blue at $\lambda =$661 nm, eosin at $\lambda =$515 nm. The degree of degradation ($R,\%$) was estimated by the loss of the dye from the solution, using the formula:

$$R,\% = \frac{(c_{\text{init}} - c_{\text{resid}})}{c_{\text{init}}} \times 100,$$

where $c_{\text{init}}$ and $c_{\text{resid}}$ are the initial and residual concentration of dye in the solution.

The possibility of using composites in the combined photocatalytic processes of degradation of soluble organic substances and generation of hydrogen from «sacrificial» reagents was investigated. Carboxylic acids ($\text{HCOOH}$, $\text{H}_2\text{C}_2\text{O}_4$, citric) were used as the «sacrificial» reagents. They act as electron donors and can be oxidized on the surface of the catalyst with the separation of $\text{H}_2$. The hydrogen generated in a gas mixture of reaction systems was collected by the procedure described in [10]. Separated $\text{H}_2$ was analytically monitored by gas chromatography using a Chromatec-Crystal 5000 device.
3. Results and discussion

Experiments have shown that the combustion of ferrosilicoaluminum in nitrogen occurs in a 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. The source of the reaction moving along the crack achieves the lateral surface of the sample, forming two reaction sources which move towards each other in the transverse direction and then are combined. A wide zone is formed, which moves along the sample to its lower end at a nearly constant velocity. Cracks are channels of accelerated filtration of nitrogen towards the reaction zone, so the rate of the combustion front along the crack is higher than the average combustion rate in the volume. In addition, along the crack the vapors of silicon and aluminum can move to the outer layers of the sample and, interacting with nitrogen, condense as nitrides. The XRD data showed that the product of the combustion of FSA in nitrogen contained the phases as follows: $\beta$-Si$_3$N$_4$, $\beta$-Si$_3$Al$_3$O$_5$N$_5$, FeSi and Fe. The presence of iron monosilicide (FeSi) is due to the dissociation of high silicide FeSi$_2$ during combustion with the simultaneous nitriding of separated silicon to $\beta$-Si$_3$N$_4$. As the XRD data showed, aluminum nitride was not detected as an independent phase, since it forms along with aluminum oxide (impurity phase in the initial alloy) a solid $\beta$-Si$_3$N$_4$-based solution, so-called $\beta$-sialon (Si$_3$Al$_3$O$_5$N$_5$) (figure 1).

To obtain a material based on silicon and titanium nitrides, metallic titanium was added to the green mixture of FSA in the amount of 5-40 wt.%. The addition of titanium in the amount of 5-20 wt. % allows combustion to be conducted in the layered mode. The propagation of a combustion wave in the layered is more preferable, since the reaction product has a structural macro- and microhomogeneity. Figure 2 shows the nitrogen content in the products and the combustion rate as a function of the titanium additive. It can be seen that after the addition of the additive to the green mixture in the amount of more than 20 wt.%, the combustion rate, as well as the amount of nitrogen absorbed is significantly reduced. This is associated with the melting of titanium and the occurrence of the so-called «melt mirror», as a result the gas filtration to the reaction zone decelerates significantly. The addition of the additive to the green mixture in the amount of more than 40 wt.% leads to the deceleration of nitrogen filtration towards the reaction zone and its termination, i.e. the combustion process stops.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{X-ray diffraction pattern of the combustion product (ferrosilicoaluminum) in nitrogen in the absence of additives: (1) $\beta$-Si$_3$N$_4$, (2) Si$_3$Al$_3$O$_5$N$_5$, (3) Fe, (4) FeSi.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Nitrogen content in products (1) and combustion rate (2) as a function of the titanium additive.}
\end{figure}
When additives are added to the green mixture in the amount of 5-10 wt.%, combustion products contain a significant amount of unreacted substances and intermediate products, which indicates an incomplete conversion of the reagents into nitrides. The best result was obtained for the case when the amount of the additive was 15-20%.

![X-ray diffraction pattern of FSA + 15% Ti (a) and FSA + 20% Ti (b)](image)

Figure 3. X-ray diffraction pattern of FSA + 15% Ti (a) and FSA + 20% Ti (b) 
(1 – TiN, 2 – β-Si₃N₄, 3 – Fe, 4 – FeSi, 5 – α-Si₃N₄).

The structure of the combustion products is uniform throughout the volume and does not contain any initial substances. Figure 3 shows the X-ray diffraction patterns of the samples synthesized. The absence of a silicotic phase is connected to its dissolution in the crystal lattice of silicon nitride, as indicated by the slight broadening of reflections of this phase. The phase composition of the combustion products depends essentially on the amount of the titanium additive. Thus, when the amount of the titanium additive in the green mixture is 15 wt.%, the predominant phase is β-Si₃N₄, while amount of the titanium additive is 20 wt.%, the predominant phase is TiN. In addition, the composites obtained have different properties. The product with a predominant silicon nitride phase is a stronger, but at the same time, brittle material, which is associated with a large amount of the ceramic phase. The reaction product with a predominant titanium nitride phase is more viscous.

Table 1 presents the evaluation of photocatalytic activity during the degradation of dyes under conditions of different photocatalytic systems. It can be seen that the highest degradation of methylene blue is observed for both samples in the presence of H₂C₂O₄ (ferrioxalate system). When eosin is disintegrated, composites with the addition of EDTA (ferricomplexonate system) exhibit a high activity. Moreover, an increase in the concentration of EDTA by an order of magnitude leads to an increase in the oxidation degree of eosin by more than 2 times.

Table 1. Degradation degree of (%) of dye solutions in the presence of iron-containing composites exposed to UV radiation (cMB=cE=10 mg/l, pH=5; mkt=200 mg; V of solution = 20 ml; τₚₚ= 20 min).

| Dye, system | No. 1 (15 % Ti) | No. 2 (20 % Ti) |
|-------------|-----------------|-----------------|
| Methylene blue + 0.001 M H₂O₂       | 32              | 39              |
| Methylene blue + 0.001 M H₂C₂O₄     | 67              | 73              |
| Eosin + 0.001 M H₂O₂                | 45              | 51              |
| Eosin + 0.001 M H₂O₂ + 2.5·10⁻⁴ M EDTA | 35              | 21              |
| Eosin + 0.001 M H₂O₂ + 2·10⁻³ M EDTA | 85              | 69              |
The obtained composites are found to be effective during the generation of H₂ from solutions of carboxylic acids (table 2). The higher productivity during the generation of H₂ from all «sacrificial» reagents is shown by composite No. 2 with the predominant TiN phase, which is a promising semiconductor compound according to [11]. The additives of methylene blue also contribute to the generation of H₂, which is demonstrated by sample No. 2. This may be due to the fact that the dye acts as a photosensitizer of the catalytic process.

**Table 2. Productivity (μmol/g·h) of the photocatalytic generation of hydrogen from solutions of carboxylic acids with the participation of composites (m_k = 200 mg; V of solution = 20 ml; t_{UV} = 20 min).**

| System\composite | No. 1 (15 % Ti) | No. 2 (20 % Ti) |
|------------------|----------------|-----------------|
| 0.05 M H₂C₂O₄ + 0.001 M H₂O₂ | 216         | 592            |
| 0.05 M H₂C₂O₄ + 0.001 M H₂O₂+MC | 281         | 829            |
| 0.01 M H₂Cit + 0.001 M H₂O₂+Eosin + 0.001 M | 127         | 438            |
| 0.1 M HCOOH + 0.001 M H₂O₂ | 20           | 84             |

Thus, iron-containing metal-ceramic composites based on silicon and titanium nitrides are promising for purification of waste water from dyes when using UV radiation. The addition of TiN to the ceramic matrix increases the activity of composites during the generation of H₂ from «sacrificial» reagents. Perspective «sacrificial» reagents are carboxylic acids (oxalic, citric) which are oxidized with the formation of H₂.

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