Effect of aluminum additives on the ignition of tungsten–teflon mixtures

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Abstract. Thermodynamic analysis and studies of combustion and structure formation of products were carried out in the powder mixtures of tungsten and polytetrafluoroethylene (Teflon, Tf) with aluminum additives. The mixture components were selected to fabricate high-density condensed products with high ignition temperature. Aluminum was used as an energetic additive accelerating the ignition process and increasing the mixture combustion temperature. In mixtures, a tungsten/Tf ratio was fixed; the aluminum content was varied according to the formula \((1 - x)(0.8W + 0.2Tf) + xAl = \text{const.}\) Mechanically activated mixtures were pressed into the samples and heated in special crucible with controlled heating rate. It was shown that an increase in the heating rate changes insignificantly the ignition temperature of systems, but strongly affects the structure of combustion products. The ignition and combustion of compositions with low aluminum content results in a large volume of gaseous products, which fly apart or form a high-porous structure. At high Al concentration, the results of experiments and thermodynamic calculations are sufficiently different that can be explained by the lack of thermodynamic data on tungsten aluminides in the used program and by the fact that real conditions of reaction are far from equilibrium and adiabatic ones. The calculated and experimental data showed that the optimal aluminum content to form melted products with a high density \(\rho(W_2C) = 17.2 \text{ g/cm}^3\) is about 10 wt %. At high Al concentration, the main combustion product (tungsten aluminide \(\text{WAl}_4\)) has the lower density \(\rho(\text{WAl}_4) = 6.6 \text{ g/cm}^3\) that is insufficient for practical application.

1. Introduction

Composites based on metal powders and polymers including the structural and functional composite materials are widely used to fabricate products of various applications. Fluoropolymers are commonly used polymeric fillers because they exhibit high thermal stability and enhanced chemical resistance. Fluoropolymers can act as a main or additional oxidizer in the energy-intensive compositions with an active metallic fuel.

One of the most effective methods to increase the reaction ability of mixtures is mechanical activation (MA) [1–3]. The MA of metal/fluoropolymer powder mixtures make it possible to prepare highly homogeneous materials owing to the formation of polymeric coatings on the surfaces of metallic particles. The appearance of these films under the action of MA may be associated with elevated concentration of fluoropolymer macroradicals [1, 4]. In addition, the MA of
metal/fluoropolymer mixtures can promote to change in the fuel properties of these composites. This is the actual problem for the chemically active metallic powders such as aluminum and magnesium.

In some cases, it is necessary to fabricate the energy-intensive materials with high density. To provide needed density, heavy metals (such as U, W, Th, Ta, Hf, Nb, etc) or heavy metal oxides (WO$_2$, WO$_3$, CuO, PbO$_2$, Pb$_3$O$_4$, etc.) are added. One of the most attractive components is tungsten because it has high density and contributes to no increase in the mixture sensibility [5]. There are limited data in literature about the kinetics of reaction between Tf and tungsten, as well as about ignition, combustion, and detonation of these mixtures. Previously, we studied the ignition process of mixtures containing tungsten, Tf, and aluminum [6]. The present work is aimed at the study of the influence of the ratio of components (tungsten, Tf, and aluminum) on the ignition parameters and composition of mechanically activated products.

2. Thermodynamic analysis of reactions for W–Al–Tf system

For thermodynamic calculations, we used the W–Tf-based compositions with aluminum added to initiate the combustion. To fabricate high-density composite, the amount of Tf should be selected in such a way to ensure high compressibility and strength and occurrence of the reaction with a high heat release. The Tf content was limited by 20 wt % in relation to tungsten mass because of its density is 2.1–2.2 g/cm$^3$. At this Tf/tungsten ratio, the aluminum content was varied according the formula:

$$(1 – x)(0.8W + 0.2Tf) + xAl = const.$$  

Results of thermodynamic calculations carried out using a THERMO program are presented in table 1.

| №  | Al, % | W, % | Tf, % | ρ, г/см$^3$ | $T_{ad}$, К | $V$, l | $S$, % (products) | $L$, % (products) |
|----|------|-----|------|-------------|-------------|--------|----------------|-----------------|
| 1  | 5    | 76  | 19   | 6.93        | 3050        | 75     | 53(C; W$_2$C) | 24(W$_2$C)      |
| 2  | 10   | 72  | 18   | 6.40        | 3130        | 99     | 2(C)         | 74(W$_2$C)      |
| 3  | 20   | 64  | 16   | 5.56        | 1985        | 106    | 71(C; W$_2$C; Al$_4$C$_3$) | 0 |
| 4  | 30   | 56  | 14   | 4.91        | 1660        | 75     | 64(Al$_4$C$_3$; W$_2$C) | 11(AI)         |
| 5  | 40   | 48  | 12   | 4.34        | 1520        | 45     | 55(Al$_4$C$_3$; W$_2$C) | 26(AI)         |
| 6  | 50   | 40  | 10   | 3.98        | 1460        | 22     | 51(Al$_4$C$_3$; AlF$_3$; W$_2$C) | 41(AI)         |
| 7  | 60   | 32  | 8    | 3.63        | 1450        | 0      | 45,5(Al$_4$C$_3$; AlF$_3$; W$_2$C) | 54,5(AI)       |
| 8  | 80   | 16  | 4    | 3.10        | 930         | 0      | 100(Al; Al$_4$C$_3$; AlF$_3$; W$_2$C) | 0 |

In the case of W–Tf mixture, the calculated adiabatic combustion temperature is sufficiently high ($T_{ad}$ =2383.5 K); the content of condensed combustion products is about 56 wt %. However, the initiation process was difficult. The addition of a small amount of aluminum (5–10 wt %) significantly decreases the mixture ignition temperature and increases the combustion temperature. Calculations resulted that the combustion products of the composition 2 may contain up to 74 % melt. The further increase in the aluminum content to 20% leads to a sharp reduction of the combustion temperature and a decrease in the content of melted products. It is worth to note that with increasing aluminum concentration and decreasing combustion temperature, the total mass of condensed products including melt increases. At the same time, the density of the initial mixture and combustion products decreases.

3. Experimental

As the initial components, tungsten powder having a particle size below 10 μm, Teflon (low-molecular weight polytetrafluoroethylene fine powder) with a dispersion below 5 μm, and aluminum powder with a particle size below 20 μm were used. The component ratios are given in table 1. The powders were mixed using an AGO-2 planetary ball mill under hexane atmosphere. The mixture-to-ball mass ratio was equal to as 1:20, a frequency of the drum rotation was 2220 rpm, and an activation time was 5 min. The powder mixtures were pressed under a pressure
of 145 MPa into cylindrical samples with a diameter of 3 mm, a height of 0.5–1 mm, and a mass of 0.01–0.02 g. The ignition and combustion processes were studied in argon atmosphere at atmospheric pressure. The ignition temperature of compositions $T_c$ was determined using an experimental setup illustrated in figure 1. The samples were suspended in the boron nitride crucible on the VR5/VR20-type thermocouple welded from 10–15 μm thick wires. The heating of samples were performed by heat irradiation from the crucible heated by an aluminum foil conducting an electric current.

![Figure 1. Schematic of experimental setup to determine mixture ignition temperature:](image)

1. BN crucible;
2. sample;
3. thermocouple;
4. heater;
5. graphite board.

4. Results and discussion

Figures 2a and 2b show the heating thermograms of samples.

![Figure 2. Heating thermograms of (a) 0.95(0.8W + 0.2Tf) + 0.05Al and (b) 0.90(0.8W + 0.2Tf) + 0.1Al mixtures at different heating rates.](image)

At the low heating rate, the sample is heated uniformly and ignited simultaneously. This results a single temperature peak in the thermograms. At the higher heating rate, there are several peaks caused by a nonuniformity of the temperature field in the sample.

Upon heating of mixtures, the fluoropolymer amorphization and melting stages take place in the pre-ignition period. In the video-recording frames, the phase transition process in samples is observed as a concentric wave propagating from the sample side surface to its center. During phase transition, the sample geometric dimensions remain unchanged. The further increase in the heating temperature above PTFE thermal destruction temperature favors a sample foaming (about 873 K) caused by the volatilization of highly volatile polymers and decomposition products (at temperatures higher than the thermal destruction temperature of 678 K). The ignition of Al + Tf mixture begins at temperatures below aluminum melting point. This is caused by the high activity of gaseous products of the PTFE destruction and lead to an initiation of the combustion of tungsten with PTFE. The additional possible reason for the mixture ignition at the temperature of about 873 K can be an exothermic effect observed near this temperature upon DTA study of PTFE, which is
explained by an oxidative thermal destruction [7, 8]. In our case, the experiments were carried out in argon and therefore, the oxidation process is not essential one. Figure 3 shows the change in the ignition temperature with increasing heating rate. The curves were plotted by the method of least squares. The analogous dependences were observed for the all studied compositions (figure 4).

![Figure 3](image3.png)

**Figure 3.** Dependence of the critical ignition temperature on the heating rate.

![Figure 4](image4.png)

**Figure 4.** Dependence of the critical ignition temperature on the heating rate (composition numbers 1–7).

Despite the wide dispersion of experimental data, the tendency to an increase in the ignition temperature for compositions with minimal and maximal aluminum concentrations is observed. This may be due to an increase in the heat conductivity of samples with high aluminum content, the formation of solid products, and a difficulty of the transfer of components in samples with low aluminum content. For all compositions, the ignition temperature of samples increases with increasing heating rate. In this case, conceivably the transition from thermal explosion mode to ignition one might occur.

In [6], we established that the main combustion product was W$_2$C. In the compositions with low aluminum content, a large volume of gaseous products is formed as a result of ignition and combustion. This is confirmed by the results of thermodynamic calculations. At 5 wt % Al, these products fly apart. In the range of 10 to 20 wt % Al, they form a high-porous structure. In the case when Al content is higher than 70 wt %, there is no ignition of samples; only small heating take place. No size and shape of samples change because the products remain condensed that is agreement with the results of thermodynamic calculations. This is associated with the fact that the Tf concentration is too low to complete the reaction and therefore, a part of metal powders remains non-reacted. According to the XRD analysis data, the main product is WAl$_4$ (figure 5).
Figure 5. XRD pattern of combustion products for 0.4(0.8W + 0.2(C\textsubscript{2}F\textsubscript{4})\textsubscript{n}) + 0.6Al mixture (composition 7).

At high Al content, the results of our experiments and thermodynamic calculations differ substantially. This is explained by the fact that there are no thermodynamic data on tungsten aluminides in the program. Thermodynamic calculation of this mixture results that one of the combustion products should be tungsten carbide (W\textsubscript{2}C), which is not detected in the experiment. The real conditions of the reaction are far from the equilibrium and adiabatic conditions. Nevertheless, the thermodynamic analysis proved to be useful to estimate the combustion temperature and gas release parameters.

5. Conclusions
The calculated and experimental data demonstrate that the optimal aluminum content to form melted products with a high density (\(\rho(W_2C) = 17.2 \text{ g/cm}^3\)) is about 10 wt %. At high aluminum concentrations, the density of the main combustion product (tungsten aluminide WAl\textsubscript{4}) is sufficiently lower (\(\rho(WAl_4) = 6.6 \text{ g/cm}^3\)) that is insufficiently for practical application.

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