Features of titanium and aluminum particles combustion

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Abstract. The results of the study of metal particles combustion process in free fall in air are presented. Titanium particles with a size of 120-540 microns and particles-aluminum agglomerates with a size of 540-660 microns were used. The characteristic times of the beginning and the end of fragmentation, the end of combustion were found with help of video filming. The laws of particles motion, in particular, their velocity and coordinate at the moment of the beginning of fragmentation, were determined. The size of titanium particles at which the fragmentation mode changes ("star" and "spruce branch") were estimated. Condensed combustion products of particles were selected and investigated.

1. Introduction

The use of metal particles in engineering and technology as a component of an energy fuel implies their transformation into combustion products - oxide particles. The practical importance of energy release or the oxide formation depend on the purpose of product. In all cases, it is required to ensure efficient conversion of the parent metal to oxide. Some high-calorie metals (Ti, Al, Zr) fragment during combustion. It is obvious that fragmentation affects both the macrokinetics of metal particle combustion and the parameters of the combustion product. Understanding fragmentation mechanism can provide key to combustion control. The fragmentation still remains one of the least studied aspects of the metal particles combustion. The choice of aluminum and titanium as objects of research is due to the following:

- Aluminum is a common structural material used in many technical objects. For a more complete understanding of the particles combustion process from a combined fuel, including aluminium, it is necessary to know the features of the combustion parameters and fragmentation of each components. Therefore, corresponding research is currently relevant.

- Titanium is in fourth place after Al, Fe, Mg in terms of prevalence in structural materials. Ti is a lightweight, high-strength and corrosion-resistant structural material. The interest in the combustion of titanium is due to two circumstances [1]. Firstly, titanium and its alloys are widely application in structural materials operating under extreme conditions [2, 3]. Second, titanium in powder form is used as a metal fuel in lighting, retarding and other pyrotechnic compositions [4, 5], as well as mixed compositions of technological combustion [6]. Technological combustion is a process carried out to obtain the target product. The areas of application of titanium are constantly expanding. Thus, relatively new applications of spherical and porous titanium powders are medicine and additive technologies [7]. There are studies in which titanium is considered as the main metallic fuel or as an additive in the composition of fuels for ramjet engines [8, 9], and in the composition of industrial explosives [10].
In all these cases, it is necessary to study the mechanism of particle combustion in order to organize a process with a high completeness of metal-to-oxide conversion. The aim of the research is to study the characteristics of combustion, fragmentation and combustion products of metallic fuel particles in air.

The paper is structured as follows: preparation of the samples, experimental technique and calculation of particle parameters methods are described in section 2; The results of experiments and calculations are presented in section 3; Section. 4 presented the conclusions derived from the results of the study.

2. Investigation of metallic fuel particles combustion

2.1. Preparation of the samples

Agglomeration of the metal takes place in the combustion wave of a mixed system including titanium as a metallic fuel. As a result, instead of the initial titanium particles, agglomerates with sizes of the order of hundreds microns fly out from the combustion surface [11]. Complete combustion of such particles is practically impossible. For the mixed systems studied in [12], the yield of product particles with a size smaller than 5 μm was less than 6% of the titanium mass in the sample. Thus, in practice, one has to deal with titanium agglomerates, and one of the topical directions is the study of the characteristics and mechanism of their combustion in air. Real agglomerates formed during the combustion of mixed systems have a wide size distribution, which significantly complicates the interpretation of the data. Therefore, in [13], [14] an approach was proposed that makes it possible to produce monodisperse burning titanium agglomerates.

For aluminum, experiments were carried out with inclusions of the following composition: 73.85% Al (fraction 0.5–1.5 μm isolated from ASD-4 powder), 26.15% active combustible binder (methylpolyvinyl-tetrazole polymer plasticized with nitro-containing compounds). The ratio between the components of the composition was selected on the basis of thermodynamic calculations based on the conditions for reaching the maximum temperature. Composition had the consistency of plasticine, was easy to form and kept their shape. The inclusions were made as follows, a fragment with size of several millimeters was separated from the composition with Al powder, weighed, then rolled into a sphere, flattened with a ruler in the form of a tablet and divided into eight parts. Each part was rolled again into a sphere, flattened and divided into four parts. Thus, one inclusion particle is 1/32 of the original weighted fragment of the composition. The scheme of particles-inclusions preparation is shown in detail in figure 1.
The range of sizes (diameters) of the investigated particles is 540–660 microns. It should be noted that this range corresponds to the actual sizes of agglomerates for aluminized fuels with strong agglomeration. At the same time, the literature data on the combustion dynamics of Al and aluminium agglomerate particles of such a large size are extremely scarce.

2.2. Calculation of particle parameters

The calculation of the particle parameters included the following:

Determining the one inclusion average mass according to the formula (1):

\[
\frac{M}{N} = \frac{m_{inc}}{n}
\]

where M is the mass of the fuel portion used to make N inclusions.

The calculation of the agglomerate initial mass \(m_{Al}\) according to the formula (2):

\[
m_{Al} = m_{incl} \cdot 0.738
\]

where 0.7385 is the mass fraction of Al in the inclusion. Typical \(m_{Al}\) values in the experiments performed were 0.00040 - 0.00060 g. With a sample volume of \(N = 10\) particles, their joint weighing is characterized by a relative error of \(\approx 2\%\) (with a balance accuracy of 0.0001 g). Theoretically, after the decomposition of the binder, the inclusion may contain some amount of carbon residues (maximum 0.09 of the inclusion mass).

Calculation of the agglomerate initial diameter by the formula (3):

\[
D_{Al} = \frac{6m_{Al}}{\pi \rho_{Al}}
\]

where \(m_{Al}\) is the initial mass of the agglomerate; \(\rho_{Al} = 2.7 \text{ g/cm}^3\) is the aluminum density.

2.3. Experimental technique

The experimental technique was as follows:

- a sample was used, consisting of a metal-free fuel-matrix, in which a certain number of particles (titanium inclusions or aluminium agglomerates) were placed;

- the sample was deposited on a quartz tube 12 mm in diameter (it played the role of a sample holder). The dimensions of the matrix \(W \times L \times H\) are approximately \(3 \times 30 \times 2\) mm. In the combustion wave of the matrix, each fragment turns into a burning particle-agglomerate. Further particles combustion occurs in air. The experimental processing methods were basically the same as in [14].

As a result, using the approach of "model monodisperse agglomerates", the combustion of large aluminium agglomerates and monolithic parent titanium particles with a diameter of 250–600 \(\mu\)m in free fall in air were studied.

3. Experimental results

3.1. Titanium particles

The "life cycle" typical for large (300–500 \(\mu\)m) titanium particles is shown in figure 2. This figure is assembled from fragments of video recording frames using the cut-and-paste technology. figure 2 shows the full track of a particle from its exit from the sample (event 0) to "disappearance" (event b).
Figure 2. Video recording of a track for a large (400 µm) Ti particle freely falling in the air [14].

The bf and ef events are the beginning and the end of fragmentation, respectively. Fragmentation occurs according to the “spruce branch” type, and in figure 2 it can be seen that between the bf and ef events marks the particle track is “shaggy” due to the shooting of small fragments. The vertical segment "50 cm" determines the scale of the image. Horizontal lines from the left of the track correspond to the track sections boundaries belonging to separate frames. In other words, it divide the track into sections that the particle flies in 1/25 s.

Let's note some of the observed features:
- before the beginning of fragmentation (above the point bf), the particle falls vertically, fragmentation causes small disturbances in its motion (deviation of the trajectory from a straight line);
- after the end of fragmentation (below the point ef), the particle velocity decreases noticeably. The particle track gradually narrows and fades, and below point b the particle is no visible. Point b is the end of combustion.

Figure 3 shows the data of the titanium particles combustion in air times depending on it size.

Figure 3. Dependences of the titanium particles burning time from it diameter.
Here, the dots-circles \( \circ \) are the data of this work for Ti with a purity of 99.38%. There are 267 points in total, 167 of these points were obtained from processing video recordings captured at a speed of 25 fps and have time determining error \( \Delta t = 0.04 \) s, 100 points were obtained from processing video records at a speed of 500 fps with the error of \( \Delta t = 0.002 \) s.

Errors in figure 3 are shown as vertical intervals, so as not to clutter up the drawing, they are drawn only at three points. Additionally, literature data for the combustion times of titanium particles are presented, namely:

- points \( \times \) - data [15] for Ti particles with a purity of 99.5% from the range of 20–125 \( \mu m \), ignited by a laser;
- \( \bullet \) - data [16] for 99% Ti particles with \( D = 240 \) \( \mu m \) and 99.99% Ti particles with \( D = 280 \) \( \mu m \), obtained and ignited in a miniature electric arc discharge;
- points \( \mathbf{\square} \) - data [17] for agglomerates of Ti 98.92% with \( D = 300, 390 \) and \( 480 \) \( \mu m \), ignited in a flameless matrix in the same formulation as in this work.

Figure 3 also shows approximation dependences of the form \( t_b(D) = AD^n \), generalizing different data sets. The parameters of the dependencies are shown in table 1, where the number of processed points \( N \) and the coefficient of determination \( R^2 \) are indicated.

| Data source | Curve designation | Approximation | D, microns | \( R^2 \) | \( N \) |
|-------------|-------------------|---------------|------------|--------|-------|
| [15]        | (\( \alpha \))    | \( t_b(D) = 1.29(D/1000)^{1.56} \) | 20–125     | -      | 9     |
| [16]        | (\( \alpha \))    | \( t_b(D) = 0.09(D/1000)^{1.45} \) | 240, 280   | -      | 2     |
| [15] [16] [17] | (\( \alpha \))  | \( t_b(D) = 5.81 \times 10^{-7} D^{2.35} \) | 20–480     | 0.997  | 9+2+3 |
| Present work | (\( \beta \))    | \( t_b(D) = (3.53 \pm 2.13) \times 10^{-6} \cdot D^{2.05 \pm 0.10} \) | 118–541    | 0.70   | 267   |
| [16] [17], Present work | (\( \gamma \)) | \( t_b(D) = (3.41 \pm 2.00) \times 10^{-6} \cdot D^{2.06 \pm 0.10} \) | 20–541     | 0.75   | 9+2+267 |

Analyzing the data in figure 3 and table 1, let’s note the following. The points obtained in this work for large monolithic particles correspond to the dependence (\( \alpha \)) constructed in [15], which generalizes the data for small monolithic particles and large agglomerates. Accordingly, the graph of dependence (\( \beta \)) built only for new points, practically coincides with the graph of dependence (\( \alpha \)) - the curves along their entire length are removed from each other by no more than 2\( \Delta t \). The available three points [15] for agglomerates are in the point cloud for monolithic particles, so that the burning times of agglomerates correspond to the burning times of monolithic particles of similar sizes. Therefore, dependence (\( \gamma \)), which summarizes all available data for monolithic particles with a diameter of 20–541 \( \mu m \), can also be applied to agglomerates. The parameters of the generalized dependence (\( \gamma \)) are close to the parameters of the dependence (\( \beta \)), since they are constructed for a dataset that coincides by 96% - 267 out of 278 points they have in common.

Among the selected combustion products, the following were distinguished:
- spherical oxide particles with diameters in the order of several tens of microns. These are the combustion remnants of fragments;
objects with an airgel structure with an overall size of up to a thousand microns, consisting of primary oxide nanoparticles chains (so-called spherules) with diameters of tens nanometers.

Figure 4. Combustion products of titanium particles
(a) spherical remnants of parent particles with size up to hundreds microns (in the case of the "spruce branch" fragmentation);
(b) spherical oxide particles with sizes of units to tens microns;
(c) objects with an airgel structure with an overall size of up to a thousand microns, consisting of oxide spherules chains with an arithmetic mean diameter of 85 nm.

3.2. Aluminum particles
The calculation of the particles - residues parameters included the following:

Determining the one particle-residue average mass according to the formula (4):

$$m_{ox} = \frac{M_{ox}}{N_{ox}}$$  \hspace{1cm} (4)

where $M_{ox}$ is the total mass and $N_{ox}$ is the total piece number of residual particles in experiments with the same agglomerates.

Calculation of the total volume of particles $\Sigma V_{ox}$ and estimation of the average density of the residual particles according to the formula (5):

$$\rho_{ox} = \frac{M_{ox}}{\Sigma V_{ox}}$$  \hspace{1cm} (5),

where $\rho_{ox}$ is the average density of residual particles, $M_{ox}$ is the total mass of particles, $\Sigma V_{ox}$ is the total volume of particles.

The collection of combustion residues was carried out using a large ($\approx 80-100$ cm) pallet made of A0 format coated paper, taking into account particles fall from a height of 3 meters. The remains were taken from the pallet immediately after the experiment. All selected particles were subjected to particle size analysis using suitable imaging techniques. Macro photography, optical and electron microscopy were used.

In most of the experiments carried out, almost complete transformation of the metal into aluminum oxide was achieved, figure 5.1. In some cases (usually for particles larger than the nominal size), there is an impregnation of metal in the oxide particle, figure 5.2.
Figure 5. Particles-combustion residues of two morphological types.
1 - Oxide particles without visible inclusions of metal;
2 - Oxide particles with holes and/or inclusions of metal.

For granulometric analysis of oxide particles-residues - determination of the diameters of the final particles from images from an optical microscope, figure 5.1 and calculation of the arithmetic mean diameter $D_{ox}$, oxide particles of a nominal size close to the average were used whenever possible. For example, the largest and smallest particles could be excluded from consideration.

4. Conclusions.
In the course of the work, the study of the combustion process of titanium particles with a size of 120-540 microns and particles-agglomerates of aluminum with a size of 540-660 microns in free fall in air was carried out. By means of video filming, the characteristic times of the beginning and the end of fragmentation, the end of combustion and the laws of particles motion, were determined. The size of titanium particles at which the fragmentation mode changes ("star" and "spruce branch") were estimated. Condensed combustion products of particles were selected and investigated.

Objects with an airgel structure, spherical oxide particles and spherical remnants of parent particles were found in the titanium combustion products.

During the experiments, the burning times of aluminum agglomerates, the size, mass and density of the final particles-residues were also determined. At a distance of about 3 meters, the agglomerates, burning, formed a residue in the form of a large spherical oxide particle with a diameter of 400–600 µm.

Acknowledgments. «The reported study was funded by RFBR, project number 20-33-90208»

Appendices
$m_{incl}$ - the one inclusion average mass;
m$_{ag}$ - agglomerate initial mass;
N – the number of inclusions;
M - the mass of the fuel portion used to make N inclusions;
$D_{AL}$ - agglomerate initial diameter;
$\rho_{Al}$ - aluminum density;
W - width;
L - length;
H - height;
$\Delta t$ - time determining error;
D - Ti particles with;
t_b - burning time;
R^2 - coefficient of determination;
m_{ox} - the one particle-residue average mass;
M_{ox} - total mass;
N_{ox} - total piece number of residual particles;
\rho_{ox} - average density of residual particles;
M_{ox} - total mass of particles;
\Sigma V_{ox} - total volume of particles.
D_{ox} - oxide particles diameter.

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