Combustion of bimetallic Ti/Al and Cu/Al fibers

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Abstract. The paper presents the results of an experimental study of the high-temperature combustion of bimetallic strands of Ti/Al and Cu/Al in air at normal pressure. It is shown that the kinetics of combustion is shown to be controlled by capillary mass transfer in metal melts. It was established, using high-speed video filming, dynamic spectrometry, that the effective maximum temperature of the processes is realized in the range of 2400 ÷ 5350 K. The burning rate is within the range of 0.26 ÷ 1.2 m/s. During the reaction conversions the atomic and molecular spectra are observed for Al, Al⁺, Cu, Cu⁺ AlO, CuO and other particles.

1. Introduction
Metals, such as Al, Mg etc. [1] and fiber metals [2, 3] are widely used as energetic fuel additives in rocket propellants, explosives. Additives of oxidized metal particles provide a high level of enthalpy and the required ballistic properties of combustion products. Understanding the burning and ignition mechanisms of metal-containing systems is important for describing new and control existing propulsion devices and weapon systems. It is of particular interest to study the behavior and mechanism of the reaction wave propagation in metallic systems using the reacting powder metal and nonmetal mixtures and the chemical compounds for the combustion synthesis of important intermetallic and ceramic materials [5, 4]. Thread-like metal composites capable of self-sustained combustion are promising for the use in special pyrotechnic devices and as simple model systems for a detailed study of the kinetics of high-temperature reactions with participation of metals [6].

The measurements [7] have shown that combustion wave propagates at a velocity of 0.15÷0.3 m/s depending on the pressure and composition of gas media and the maximum process temperature is in the range of 2600÷3720 K. The kinetics of combustion is shown to be controlled by capillary mass transfer in metal melts. The effects of regular acoustic emission were found during combustion of the Ni-Al system [8].

In the present work, the thermal, structural and emissive dynamics of fiber-like Cu-Al and Ti-Al composites during ignition and combustion in air is studied.

2. Materials methods
The metal fibers with a purity of 99.5wt.% of the initial substance were used for studies: Ti (diameter ø = 0.42 mm), Al (ø = 0.4 mm), Cu (ø = 0.3 mm). The composites were the mutually twisting fibers in proportion: Ti+(35÷40) wt. % Al; Cu+(35÷40) wt. % Al. The technique of the experiments is described in the work [6]. The samples of composites were fixed in copper electrode holders located at
a distance of 20 mm from each other. Combustion was initiated by short passing an electric current through the sample before melting and breaking of the central part. Two reaction waves spontaneously propagated along the sample towards the electrodes. Combustion was conducted in oxidizing (air) gas media at a pressure of \( P = 10^4 \div 1.01 \cdot 10^5 \) Pa.

Within 1 ms, after the breakage of the sample, the supply of voltage to the electrodes was automatically stopped. Specific electric power of ignition \( \approx 1.2 \) and \( 1.4 \) W/mm\(^2\) correspond for TiAl, CuAl. Delay time of ignition \( \approx 2.4 \) and 10 s correspond for TiAl, CuAl.

The combustion process was supported by synthetic and oxidative exothermic reactions:

\[
Me + aMe' \rightarrow Me_aMe'_b (s, l); bMe + cMe' + dO_2 \rightarrow Me_bMe'_c O_d (s, l, g),
\]

where \( a, b, c, d \) are the stoichiometric coefficients of chemical compounds, the indexes \( s, s, l, g \) corresponds to the solid, liquid and gaseous state of the substances.

The processes were monitored using high speed video recording (Motion ProX-3, the frame frequency was up to 10,000 s\(^{-1}\), and by dynamic monitoring of emission spectra (HR 4000-Ocean Optics spectrometer, range of wavelengths \( – 200 \div 1100 \) nm, optical resolution \( – 0.2 \) nm). Atomic emission lines and molecular bands of spectra were identified using NIST data [9].

The combustion temperature was determined by method of spectral pyrometry [7]. The resulting spectra were converted to Wien's coordinates that allowed finding the temperature along the slope angle of a curve piece with a linear shape.

3. Results and discussion

The studies have shown that there is the complete melting of initial materials, intermetallic and oxide reaction products in the combustion wave of composites, and the wave propagation is accompanied by specific hydrodynamic and emission effects.

3.1 System Al-Ti

According to the video data, at the heating stage, the aluminum wire is melted in the central part of the sample (figure 1a, 1) and further melting propagates in the directions to the electrodes. Comparing the spectrometry and video recording data, it follows that the stage of spreading of aluminum over the surface of titanium is realized at a temperature of 1924 K, the plateau on the temperature curve the figure 3a, comparable to the melting point of titanium - 1943 K. A further increase in temperature leads to a partial melting of titanium (figure 1b), an exothermic interaction of the components of the system begins, by reaction diffusion, which spreads to the periphery as a wave from the site. Further, an increase in temperature of 1210 K in 18 ms to a value of 3087 K leads to the initiation of reaction waves from the center of the sample. It should be noted that before the rupture, the central part of the sample is gradually thinned (figure 1c). Here, an increase in temperature to 3087 K leads to the complete melting of the condensed phases — the melt formed is gradually moving towards the electrodes (figure 1d). The combustion wave of the composite Ti/Al is a liquid drop with a diameter of \( d=1\div2 \) mm (figure 1d), inside of which there is the exothermic interaction of Ti and Al melts with the participation of an external gas medium. The speed of movement of droplets along the sample in the range of 3087 ÷ 2577 K is more than 1 m / s (figure 1c, d). Further, when the influence of external heating is leveled, the average speed falls within the interval \( U_f = 380 \div 420 \) mm / s. Here, the pyrometric temperature (\( T_p \)) monotonously decreases in the range of 2660 ÷ 2530 K (figure 2a). The latter value corresponds to the moment of contact of the drop with the copper electrode-holder. In heterogeneous systems the combustion rate is usually determined by the approximation relation:

\[
U_f \sim r^{-1} \cdot (a \cdot D)^{0.5}
\]

where \( r, a, D \) are the heterogeneity scale, the coefficients of thermal conductivity and mass transfer.
Figure 1. Frames of video recording of Ti-Al composite combustion. Air, P = 1.01 \cdot 10^5 \text{ Pa.}
(a, b) initial state, (c) ignition - source stopped, (d) – propagation of combustion,
(1) local aluminum melting zone, (2) zone of melting Ti, (3) gas-dust layer (flame), (4) drop, (5) high brightness area in flame.

Figure 2. Chronogram of the temperature was determined by method of spectral pyrometry (a) and emission spectra of Ti-Al composite during ignition and combustion (b). Air, P = 1.01 \cdot 10^5 \text{ Pa; (*) time of ignition, (**) the end of combustion.}

Taking into account the experimental and reference values of the parameters for the systems studied (r~a/2 \approx (0.5\pm1) \cdot 10^{-4} \text{ m}, a(Al) \sim 7 \cdot 10^{-6} \text{ m}^2/\text{s}, a(Ti) \sim 7 \cdot 10^{-6} \text{ m}^2/\text{s} [10]), it follows that the value $D \geq 10^{-3} \div 10^{-2} \text{ m}^2/\text{s}$ is many orders of magnitude greater than the values of the diffusion coefficients in the melts of metals and oxides ($\sim 10^{-9} \div 10^{-8} \text{ m}^2/\text{s}$ [10]). This fact indicates the significant role of the melt convection during combustion. This conclusion (figure 3) is confirmed by the dynamics of inhomogeneities in the luminance field of thermal emission from the surface of reacting melts, where there is the development of the flows in the form of a fluid circulation cells (individual vortices, the net of ordered cells, typical for the capillary convection of liquids near a free surface [11]. Velocity of flows is a $0.05 \div 0.1 \text{ m/s}$. On the surface of the reaction droplet (figure 3a, a'), there is a translational motion of the metal droplets, their collision and coalescence. The frames (figure 3c, c', c'') illustrates the dynamics of the formation of polyhedra on the surface of a liquid drop during the reaction process.
Figure 3. Structure of capillary flows on the surface of a drop of reacting melts of Ti-Al composite.
Air, P = 1.01·10^5 Pa. (1) local reaction source, (2, 3) vortex flows, (4) a set of convective polyhedral cells, (5) jet stream.

Video analysis has shown that the propagation of the reaction wave is accompanied by a relatively uniform thermal evaporation of the material from the surface of the drop (figure 1c, d). Evaporation is supplemented by jet ejections from local reactionary foci, where, obviously, melt boiling occurs (figure 3). As a result, a gas-dust flame is formed near the surface of the droplet, where the evaporating components react with each other, as well as with the surrounding gaseous medium, to form oxide compounds. The latter is confirmed by the observation of weak molecular bands (figure 2b), corresponding to aluminum monoxide AlO. Also the presence of bright, relatively droplet, areas in the flame (figure 1d, figure 3), where an increase in the intensity of the glow occurs due to the exothermic oxidation of aluminum vapor. The flashing of the AlO bands is realized in the range of combustion temperatures - 2700 ÷ 3070 K. In the process of ignition, on the background of the continuous spectrum, resonant Al lines appear: 669.93 nm, Na: 588.99, 589.92 nm, K: 765.91, 769.30 nm, which, in the process of sample breaking, are supplemented with Al lines: 394.4, 396.1 nm (figure 2b). It should be noted that values of spectral temperature is due to the partial contribution of radiation of the liquid drop and flame radiation (the gas-dust phase). At the moment of ignition the emission intensity of the gas-dust phase is maximal and the value of $T_p$ is close to the temperature of the gas-dust phase. At the moment, when combustion stops, the brightness of the gas-dust phase is minimal and $T_p$ approaches the temperature of the liquid drop.

3.2 System Al-Cu
The combustion of the system (figure 4) can be divided into the following stages: heating, which includes melting aluminum wire in the central part of the sample, movement of the melt along the copper surface from the center to the periphery, at a distance of ~ 1.5 mm, followed by sticking to the droplets under the action of surface tension forces. Further, in the center of the composite, a heating maximum arises, which leads to the next stage, the thermal explosion. Comparison of dynamic spectrometry data (figure 5a) and video showed that when the temperature reached 1337 K (the melting point of copper was 1356 K), the system was instantaneous, within 9 ms, the system was heated to a temperature of 5357 K. The central part of the sample explodes, initiating reactionary waves that propagate along the composite in the direction of the electrodes - the burning stage. The combustion wave is a liquid drop (figure 6), inside of which there is the exothermic interaction of Cu and Al melts with the participation of an external gas medium.
Figure 4. Frames of video recording of Cu-Al composite combustion. Air, $P = 1.01 \times 10^5$ Pa. (1) drop of Cu, (2) twisted wires of Cu/Al, (3) gas-dust layer (flame).

The average velocity of the drops moving along the sample is as follows: $U_f > 1000$ mm/s (in the range of $T_p = 5357 \pm 3042$ K) and $U_f = 460 \pm 580$ mm/s, here $T_p$ decreases monotonically in the range $3010 \pm 2618$ K (figure 5a).

The propagation of combustion is accompanied by evaporation of the components of the drop with the formation of a gas-dust layer above it. The dispersed components of the gas-dust phase are the condensates of primary steams or the products of their oxidation (figure 5b, figure 7). Evaporation proceeds uniformly over the surface of the drop, also is supplemented by jet streams from local reaction sources (figure 6), where, obviously, melt boils. The composition of recorded optical emission is a superposition of continuous and selective spectra (lines Al, Al$^+$, Cu, Cu$^+$, Na, K and molecular bands of AlO, CuO (wavelength range of 488.24÷451.8 and 605.93÷616.16)) (figure 7). The continuous spectrum is determined by the thermal radiation of the drop and particles of the gas-dust phase. The intensity of the AlO and CuO bands is maximal during the ignition of the samples and decreases as the combustion propagates (figure 5). Comparing the spectrometry and video recording data, it follows that the change in the intensity of the AlO bands and emission of the gas-dust phase during combustion occurs symbatically. When combustion stops, the brightness of the gas-dust phase is minimal and $T_p$ approaches the temperature of the liquid drop – 2636 K.

Figure 5. Chronograms of the temperature was determined by method of spectral pyrometry (a) and intensity of the AlO emission band ($\lambda = 504 \div 530$ nm) (b) during the combustion of Cu-Al composite. Air, $P = 1.01 \times 10^5$ Pa; (*) time of ignition, (**) the end of combustion.
Figure 6. Structure on the surface of a drop of reacting melts of Cu-Al composite. Air, $P = 1.0 \cdot 10^5 \text{ Pa}$ (1) drop, (2), (2') moving of reaction zone, (3) high brightness area in gas-dust layer (flame), (4) jet stream.

Figure 7. Emission spectra of Cu-Al composite during ignition and combustion. (1, 2) ignition, (3) propagation of combustion.

4. Concluding Remarks

The combustion wave of a twisted wire is a high-temperature liquid drop 1÷2 mm in diameter, propagating along the sample at a velocity of 380÷580 mm/s. Initiation occurs when the melting point of the more refractory component is reached - Ti and Cu. The exothermic reaction of Al with Cu and Al with Ti melts develops in the drop, and above the surface of the drop a gas-dust phase containing steams and condensates of Al is formed. Combustion is supplemented with oxidative reactions with the formation of AlO, CuO and oxide condensates in the gas-dust phase. The maximum spectral combustion temperature increases from 2500 to 5350 K. Combustion is accompanied by the effects of capillary convection of melts.

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