Combustion of composite Ni–Al fibers

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Abstract. Thermal, structural and emissive characteristics of the combustion of metal composite Ni-Al fibers in an inert and oxidizing media are studied using high-speed video recording, dynamic spectrometry and Langmuir probe. The measurements 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 emission of nonequilibrium gas plasma and the spontaneous electric polarization of reaction wave are found, where the difference in electrical potentials of the condensed and gas-dust phases can exceed (2÷3) 10³ V.

1. Introduction
Understanding the behavior and mechanism of combustion of metal-containing systems is important for solving urgent problems of increasing the energy release and the combustion rate of composite rocket fuels by adding powders and fiber-like metals (Al, Mg, Al-Ni, Al-Pd, etc. [1-4]). A particular interest in the study of high-temperature reaction waves in metal-containing powder mixtures is caused by their use for the synthesis of functional inorganic materials [5-7]. 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.

In this work, the thermal, structural and emission dynamics of fiber-like Ni-Al composites combustion in an inert and oxidizing gaseous media is studied.

2. Materials and methods
Composites were prepared by twisting of aluminum and nickel wires with the ratio Ni+(25÷30) wt.% Al. The diameter of the wires was 0.3 mm (Ni) and 0.4 mm (Al), and the purity of the materials was not less than 99.5 wt.% of the main substances.

The schematic of the experiments is shown in figures 1 and 2. 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 (figure 1). Two reaction waves spontaneously propagated along the sample towards the electrodes. Combustion was conducted in inert (Ar) and oxidizing (air) gas media at a pressure of \( P=(10^4÷1.01) \times 10^5 \) 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 \( \approx 1.0 \) W/mm².

The combustion process was supported by synthetic and oxidative exothermic reactions:
where $a, b, c, d$ are the stoichiometric coefficients of chemical compounds.

Combustion was controlled by video recording (Motion Pro x-3, frame rate is up to 10000 fps, spatial resolution is 10 $\mu$m) and by dynamic monitoring of emission spectra (HR 4000-Ocean Optics spectrometer, range of wavelengths – 200÷1100 nm, optical resolution – 0.2 nm). Atomic emission lines and molecular bands of spectra were identified using NIST data [8].

The combustion temperature was determined by method of spectral pyrometry [9, 10]. This method is based on the fact that in certain wavelength intervals the thermal spectrum of condensed substances is similar to that of a gray body. When the condition $\lambda \cdot T \leq 3 \cdot 10^6$ nm·K is satisfied, the emission spectrum within these regions is described by the Wien function:

$$\ln I(\lambda, T) + 5 \cdot \ln \lambda = -(h \cdot c \cdot k^{-1}) \cdot (T \cdot \lambda)^{-1} + \ln(e \cdot 2\pi \cdot c^2 \cdot h),$$  \hfill (1)

where: $I(\lambda, T)$ – spectral intensity of emission; $\lambda$ – wavelength; $T$ – temperature, $e = \text{const} \leq 1$ – emissivity factor; $c$ – speed of light; $h, k$ – Planck’s and Boltzmann’s constants, respectively.

The spectral data obtained in this work were analyzed in the coordinate plane: $x = \lambda^{-1}$, $y = \ln I(\lambda, T) + 5 \cdot \ln \lambda$. For the wavelengths with the best linear dependence $y = f(x)$ corresponding to relation (1), the data were approximated by the function $y = ax + \text{const}$. The value $a$ was used to calculate the temperature by the formula:

$$T = (h \cdot c \cdot k^{-1}) \cdot a^{-1}.$$  \hfill (2)

The relative error in the determination of temperature, related to the scatter of the experimental points around the approximating straight line, did not exceed 3%. For the pyrometry of combustion, an interval $\lambda = 500÷575$ nm was used, which was selected on the basis of test measurements of the temperature of Ni, Fe and Mo wires during melting due to the heating by electric current under Ar. In this interval, the experimental temperatures Ni – 1740 K, Fe – 1789 K and Mo – 2905 K have a minimum deviation from the known melting points: Ni – 1726 K [11], Fe – 1812 K [11] and Mo – 2890 K [11].

![Figure 1](image1.png)  
**Figure 1.** Schematic of combustion of Ni-Al composite. (a) initial state, (b) moment of ignition, (c) combustion, (asterisk) direction of combustion.

![Figure 2](image2.png)  
**Figure 2.** Experimental setup for Langmuir probe measurements. (1) probe, (2) ac voltage source, (3) reference resistance.

Emission plasma of combustion was dynamically controlled according to the schematic shown in figure 2. The measurements were carried out using an Langmuir probe in the form of a wire copper spiral: internal diameter – 4 mm, wire diameter – 0.2 mm. The composite sample was placed inside the
spiral along the axis. Relative to the sample, an alternating voltage \((V_s=15\, V, \nu=500\, \text{Hz})\) was supplied to the probe. During combustion, an electrical current was observed in the measuring circuit of the probe, indicating the emission of gas plasma. The signals of current \((i_z=V_z R_c^{-1}; V_z – \text{voltage on the reference resistance } R_c)\) and the voltage between the probe and the spiral \((V=V_s-V_2)\) were transmitted via an analog-to-digital converter to the computer. The electron temperature of plasma was determined using the Langmuir method [12]. The method is based on the assumption of the Maxwellian electrons energy distribution. In this case, the quantities \(i_z\) and \(V\) in the interval of \(V\geq0\) can be expressed by the relation:

\[
\ln i_z = C + V \cdot e \cdot (k \cdot T_e)^{-1},
\]

where \(e\) – electron charge, \(k\) – Boltzmann’s constant and \(C\) – const.

The obtained data were analyzed in the coordinate plane: \(x=V, \, y=\ln i_z\). In the interval \(V\geq0\), the experimental dependence \(y=f(x)\) was approximated by the function \(y=a \cdot x + \text{const}\). Taking into account the value \(a\) and relation (3), the electron temperature of emission plasma was calculated by the formula:

\[
T_e = e \cdot (k \cdot a)^{-1}.
\]

The temperature calculation error due to the scatter of the experimental points around the approximating straight line did not exceed 10%.

3. Results and discussion

3.1. Hydrodynamic effects of combustion

According to the video recording data, the combustion wave of the composite is a liquid drop with a diameter of 1÷2 mm, inside of which there is the exothermic interaction of Ni and Al melts with the participation of an external gas medium. The average velocity of the drops moving along the sample is as follows: 

\[
U_f = 150 \div 200 \, \text{mm/s (Ar)}, \quad U_f = 250 \div 300 \, \text{mm/s (air)}.
\]

Taking into account the characteristic melting time of the wires \((t_m \sim a \cdot U_f^2)\) and the reaction conversions of the composites \((t_c \sim D^2 \cdot d^{-1})\) in the combustion wave, the effective mass transfer coefficient of the reagents (Ni, Al, O) inside the liquid drop can be estimated by the formula:

\[
D \approx r^2 \cdot U_f^2 \cdot a^{-1},
\]

where \(d\) – average diameter of the wires or the radius of the drop, \(a\) – effective thermal diffusivity of the composite.

Taking into account the experimental and reference values: 
\(U_f=150 \div 300 \, \text{mm/s}, \quad d=0.3 \div 2 \, \text{mm}, \quad a(Al) \sim 7 \cdot 10^{-5} \, \text{m}^2/\text{s} \,[13], \quad a(Ni) \sim 1 \cdot 10^{-6} \, \text{m}^2/\text{s} \,[13]\), it follows from relation (5) that the value \(D>10^{-5} \div 10^{-3} \, \text{m}^2/\text{s}\) is several orders of magnitude higher than the limiting permissible coefficient of molecular diffusion in metal melts or oxides \(\sim 10^{-8} \div 10^{-9} \, \text{m}^2/\text{s}\) [13]. The latter indicates dominance of the convective mechanism of transfer of reagents in the combustion wave. The presence of convection is confirmed by local jet streams, vortex flows, and nearly regular polyhedra on the surface of the liquid drop during the reaction process (figure 3). The velocity of jet streams reaches 0.2 m/s. The observed structural inhomogeneities reflect the circular microflows of melts which are typical for capillary convection of liquids near a free surface [14].

3.2. Emission effects

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. In an inert medium, evaporation proceeds uniformly over the surface of the drop. In air, evaporation is supplemented by jet streams from local reaction sources, where, obviously, melt boils (figure 4). During \(5 \cdot 10^{-5} \div 10^{-3} \, \text{s}\) the emission intensity of the jet increases sharply, which is caused by an increase in the temperature of the gas-dust
phase due to the exothermic reaction of steam oxidation. There is an effect of twisting jets around the drop, which indicates a strong electrical polarization of the system: drop and gas-dust phase. Taking into account the balance of Coulomb and centrifugal forces and the conservation of electric charge in this system, it follows that the difference in the electric potentials of the drop and gas-dust phase can reach the value $\geq (2\div3)\times10^3$ V.

Figure 3. Structure of capillary flows on the surface of a drop of reacting melts of Ni-Al composite. Ar, $P=10^4$ Pa. (1) a set of convective polyhedral cells, (2) vortex flows.

Figure 4. Frames of video recording of Ni-Al composite combustion. Air, $P=1.01\times10^5$ Pa. (1) reaction zone; (2) local reaction source; (3, 3', 3'') jet stream; (*) the direction of combustion propagation.

The composition of recorded optical emission is a superposition of continuous and selective spectra. The continuous spectrum is determined by the thermal radiation of the drop and particles of the gas-dust phase. During combustion under Ar, the selective spectrum contains atomic lines of Al: 669.93 nm, Na: 588.99, 589.92 nm, K: 765.91, 769.30 nm. During combustion under air, these lines are supplemented with molecular bands of AlO monoxide with a wavelength range of 435÷555 nm and lines of Al: 394.4, 396.1 nm. The intensity of the AlO bands is maximal during the ignition of the samples and decreases as the combustion propagates (figure 5, curves 1, 2). 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.

The pyrometric combustion temperature in an inert medium is practically constant during the reaction process: $T_p=2600\div2660$ K (figure 6, curve 3). Under air, a higher temperature is recorded (figure 6, curves 1, 2), which decreases monotonically in the range of $T_p=3720\div3300$ K ($P=1.01\times10^5$), $T_p=3275\div2475$ K ($P=10^4$ Pa). The change of $T_p$ is explained by the variable partial contribution of radiation of the liquid drop and the gas-dust phase to the pyrometric temperature. 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. When combustion stops, the brightness of the gas-dust phase is minimal and $T_p$ approaches the temperature of the liquid drop.
Figure 5. Emission spectra of Ni-Al composite during ignition and combustion. (a) Ar, $P=10^4$ Pa, (b) air, $P=10^4$ Pa. (1, 2) ignition, (3) propagation of combustion.

Figure 6. Chronograms of the pyrometric temperature (a) and intensity of the AlO emission band ($\lambda=504\div530$ nm) (b) during the combustion of Ni-Al composite. (1, 1') air, $P=1.01\cdot10^5$ Pa; (2, 2') air, $P=10^4$ Pa; (3) Ar, $P=10^4$ Pa. (*) time of ignition, (**) the end of combustion.

According to the probe measurements, the electron temperature of ionized gas $T_e$ in the combustion wave significantly exceeds the pyrometric temperature and reaches values $(6\div9)\ 10^3$ K (Figure 7, curve 1) during combustion under Ar and $(8\div18)\ 10^3$ K during combustion under air (Figure 7, curve 2). This indicates a nonequilibrium excitation of gases during the reaction conversions of composites.

Figure 7. Chronogram of the electron temperature of emission plasma during the combustion of Ni-Al composite. (1) Ar, $P=2\cdot10^3$ Pa, (2) air, $P=2\cdot10^3$ Pa. (*) time of ignition, (**) the end 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 150÷300 mm/s. In an inert medium (Ar), the exothermic reaction of Al and Ni 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 under air is supplemented with oxidative reactions with the formation of AlO and oxide condensates in the gas-dust phase. The maximum pyrometric combustion temperature increases from 2600 to 3720 K during the transition from an inert to an oxidizing medium. Combustion is accompanied by the effects of capillary convection of melts, strong electrical polarization of the gas-dust phase relative to the reactive liquid drop (more than 2÷3 kV), and nonequilibrium emission of gas plasma with an electron temperature of (6÷18) 10^3 K.

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