Qualitative characteristics of the results of experimental studies of initiation and combustion of mechanically activated mixtures of aluminum and copper oxide powders

S Yu Ananev$^{1,2}$, B D Yankovsky$^1$ and A Yu Dolgoborodov$^{1,3}$

$^1$ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
$^2$ Moscow Institute of Physics and Technology, Institutski Pereulok 9, Dolgoprudny, Moscow Region 141700, Russia
$^3$ Semenov Institute of Chemical Physics of the Russian Academy of Sciences, Kosygina 4, Moscow 119991, Russia
E-mail: yiy2004@mail.ru

Abstract. We present new experimental results on the initiation and the combustion velocity of mechanically activated compositions based on micron aluminum and copper oxide powders mixtures at a relative density of 40–60%. The initiation of combustion were produced by electric-spark method with a power input of 1.5–6.0 mJ during the 1.2 $\mu$s. Diagnosis was performed by means of the photographic registration process in cylindrical glass tubes with a diameter of 3.5–8.5 mm. Depending on the initiation energy, dose of activation and the tube diameter combustion rate is estimated in the range 30–90 m/s, and the induction period 20–2200 $\mu$s. Spread of combustion is characterized as a consecutive chain of microexplosions in contact points of reagents.

1. Introduction
Experimental data on combustion of reactive powder mixtures of metals oxides with metals have considerable variation on values of combustion speeds [1]. It results in a lack of unambiguous interpretation of the mechanism of reaction spread. Considerably the variation can be caused by both different conditions of preparation of samples and different conditions of initiation, reaction behavior and ways of measurement. At the same time, there is an opinion that for combustion of such mixtures there is no “an effect of memory of entry condition”. Only the current parameters can be essential: size of particles and porosity of sample. Nevertheless, we have paid the main attention to a research of influence of entry conditions of initiation.

2. Details of experiments
2.1. Initial components and activation
In the present work, the study of combustion of mixture of aluminum and copper oxide powders by means of photography the glowing of products of combustion was conducted. The samples were placed in glass cylindrical tubes, which, in turn, were placed in vessels with water having
Figure 1. (a) Experimental scheme: 1—dark (no combustion) part of glass tube containing the mixture; 2—glass vessel with water; 3—light (there is a combustion) part of tube; 4—a boundary between dark and light parts of tube; 5—a spark gap; 6—electrodes. (b) The image of Al–CuO mixture after mixing in a ball mill.

transparent walls [figure 1(a)]. As initial materials, aluminum pyrotechnic powder (PP-2 brand, the flat particles with linear sizes of 50–100 µm and 2–5 µm thick) and CuO copper oxide powder (pure for analysis, particle sizes 20–50 µm) were used. Components were mixed in the stoichiometric proportion of Al–CuO (18.5 : 81.5).

Activation of components was carried out in two spherical mills of vibration (Aronov’s) type and of planetary one (Activator-2SL). For preventing reaction, hexane was added into mixture, and activation was carried out by 60-seconds cycles. At that, there was a crushing and mixing of components. Time of activation was changed from 2 to 20 min. The activated mixture was filled up in a glass tubes with a diameters of 3.5, 5.5, 8.5 and 100 mm long. The porosity of mixtures was 40–60%. The obtained powders represented a polydisperse mixture of large conglomerates consisted from flat fragments of Al particles (about 10 µm) with crushed to submicron size CuO particles [figure 1(b)]. Owing to different strength characteristics of material, dispersion in sizes and a form of particles, the conglomerates were formed in a form of the disordered structures with numerous, but separate, points of contact of components. These points of contact of components, presumably, can serve as primary centers of chemical interaction.

2.2. Initiation

The initiation of the combustion was carried out by spark at the top end of the tube. The spark gap between the wire electrodes with a diameter of 0.5 mm was 0.15–0.20 mm. The energy in the spark is in the range of 1.5–6.0 mJ was regulated by changing the current amplitude [figure 2(a)]. It should be noted, that approximately the same amount of energy released during the combustion of 1 µg of used mixture. The duration of the current pulse in the spark was 1.2 µs at the base. The moment of sparking was used for synchronization of high speed gated intensified camera Cordin 222-16. The camera allowed to get up to 16 photos of the process at a predetermined time points [figure 2(b)].
3. Experimental results
In the photos, a boundary between dark and light parts of a tube (i.e., between initial material and combustion process zone) was fixed [see figures 1(a) and 2(b)]. This boundary was identified with some stage of chemical interaction characterized by a certain temperature. In literature this stage is characterized as adiabatic thermal explosion. In our case the speech can go about thermal explosion in the neighborhood of points of contact of components. The long luminescence behind the boundary in process of its movement is caused by hashing and interaction of initially not contacting parts of components. Time interval between the moment of initiation and formation of boundary is usually called the induction period. Movement of this boundary in time was taken for the speed of mixture combustion in a tube.

Approximation of experimental points of the corresponding $x$–$t$ chart of boundary movement gave value of speed (figure 3). As a rule, the approximation of 6–12 experimental points by linear dependence in median area of a tube had a determination coefficient not worse 0.98. The point of intersection between the linear approximation of the $x$–$t$ chart of boundary movement with abscissa axis defined value of induction period. In our experiments, values of the combustion

Figure 2. (a) The oscillogram of the current pulse in the spark. (b) The characteristic photos of dynamics of mixture combustion in the tube.

Figure 3. Typical $x$–$t$ charts of movement of boundary between light and dark parts of a tube.
speed of mixture were in the range of 30–90 m/s. Values of the period of induction were in the range of 20–2200 µs. Values of these parameters in each case depended on a combination of entry conditions (mill type, activation dose, mixture porosity, tube diameter, energy in a spark and so on). At considerable times of a delay of light manifestation of reaction the electric-spark introduction of energy during 1 µs can be characterized as “instant”. Finding dependence between combustion speed and each of parameters of entry conditions demands significantly the bigger volume of experimental data and, in particular, bigger number of photos of the initial site of a tube. Therefore, we will pay attention to some facts:

(i) The photography of boundary at the time of its appearance is very successful, but rare event. In this case it is possible to establish the facts of formation of border near a point of initiation and her acceleration from zero speed, see red points in figure 3. In the greater part of experiments it was observed formation of boundary at a distance from a point of initiation and its movement with a final speed without preliminary acceleration. Perhaps, the effect of acceleration of boundary takes place only at certain combinations of entry conditions. So, for example, it was defined that mixtures with a dose of activation, optimum on ignition temperature, light up with the smaller period of induction.

(ii) To start the reaction of Al oxidation, the oxygen atoms emitted at thermal decomposition of CuO are required. In the order of value in the initiating spark is emitted the amount of energy sufficient for decomposition of only 1 µg of copper oxide for the purpose of release of free oxygen. Such amount of substance contains approximately in the volume of 0.4 mm³. It only ten times more the volume of a gap between electrodes. At the same time, the volume of area what warms up during a spark power contribution, does not exceed 0.03 mm³ (estimated on aluminum thermal diffusivity). On the other hand, the gap between electrodes is about 30 times less than diameter of a tube. In total, this fact indicates the realization of almost pointed initiation of chemical interaction.

(iii) It was recorded that spark initiation of chemical interaction at an open end face of a tube demands more energy, than at the closed end face. It demonstrates the existence of critical value of energy density for interaction initiation.

(iv) The mixture, moistened with water by means of capillary effect, is not amenable to initiative even at tenfold increase in spark energy release. At the same time, in the same mix, but subjected to consolidation, there is a chemical self-heating, up to moisture boiling up. It may be the evidence of the decline, due to wetting, in the number of points of components contact, perspective to start interaction, and of the increase heat losses at heating of excess moisture.

(v) Glass tubes of average diameter often kept an initial form after mixture combustion though became covered by net cracks. On an internal surface of their walls balls of copper (with a diameter up to 2 mm) and agglomeration of oxide of aluminum were condensed (figure 4). It demonstrates a thermal form of chemical energy release. Initiation of chemical interaction of components in tubes of small diameter did not lead to combustion. In a tube of large diameter combustion happened in the steam-gas cover which was formed at evaporation of the water getting through the cracks in a glass (figure 5). Such influence of the cross size can be explained with change of integrated thermal balance due to square growth of chemical energy release at increase in a tube diameter, in comparison with the linear growth of heat losses in a wall.

(vi) The boundary between the dark and glowing areas of a tube in our experiments often does not keep a flat form during the spread of chemical interaction (figure 6). Moreover, the arising primary distortions of a form of boundary of the glowing area continue to exist, as a rule, in the form of dark inclusions. The similar nature of distribution of chemical reaction was investigated in [2,3] and characterized as a thermal percolation. In case of our
Figure 4. The images of (a) net cracks on a glass tube wall, the condensed products (Cu and Al₂O₃) of combustion (b) at a tube end face and (c) on the inner surface of the tube.

Figure 5. The photos of combustion in the steam–gas shell under the destruction of the glass tube of large diameter.

mixture particles of aluminum powder form a percolation grid due to significantly bigger heat conductivity (> 300 times) in comparison with heat conductivity of copper oxide. An initial diversity of points of contact of components particles, as perspective centers of chemical reaction, promotes the observed heterogeneity of a luminescence of combustion area.

(vii) In the analysis of a dispersion in the obtained values of combustion speed of heterogeneous compounds by different authors it is necessary to pay attention to a measurement method. For this purpose we carried out comparative diagnostics of a flow of chemically reacting components by different methods. The hinge plate of the initial compound of bulk density in mass of 1 g was initiated in an end face of the rectangular channel 105 mm long and a section of 10 × 10 mm² with a cross magnetic field [figure 7(a)]. As a markers of time the signals of piezoelectric transducers, potential and current electrodes and also photos were used. It is obvious that the specific signal is connected to the specific parameter of the
Figure 6. Photos of inhomogeneities of the luminescence as a result of the chemical interaction spread in the form of thermal percolation.

Figure 7. (a) The diagram of the experimental assembly of combustion of a mixture components in the rectangular channel with a cross magnetic field: 1—mixture; 2—flow; 3—magnetic system; 4—potential electrodes; 5—the current electrodes; 6—piezotransducer. (b) $x$–$t$ charts of response of different sensors: 1—movement of the front of density; 2—movement of the front of the burning clusters; 3—movement of the front of plasma of reaction products; 4—movement of a radiating flow outside the channel.

environment and process statuses. Therefore, different sensors can react to parameters of the different stages of combustion process, proceeding with different speeds and in different
time points. Resulted $x-t$ charts for response of different sensors are provided in figure 7(b).

For this experiment was recorded mass flow rate of 654 m/s, speed of the burning clusters of 449 m/s, speed of plasma of reaction products of 149 m/s, speed of a radiating flow outside the channel of 265 m/s. At the same time, duration of the expiration of the reacting flow exceeded 1 ms. The distinction between the heterogeneous compounds burning and homogeneous energetic materials burning express in an inequality of speeds of different processes.

4. Conclusions

The above data allow concluding:

- For realization of the “instant” (about 1 µs) initiation of mixture, the densities of insertion energy and chemical energy release must be approximately equal.
- Spread of chemical interaction in porous mixture of aluminum and copper oxide powders occurs in the form of thermal flash at contact points of components.
- The leading mechanism of the distribution of the glowing reaction front as a consecutive chain of microflashes is, apparently, the thermal percolation based on aluminum powder flat particles.
- The structure of a percolation grid is set, in many respects, by a dose of mechano-activation and way of laying mixture in a tube.
- The energy of chemical reaction turns, generally, into internal energy of reaction products.
- The speed of propagation of thermal explosion front is several tens of meters per second.
- Determined value of the “combustion speed” is tied to the speed of change of that parameter of process which is diagnosed by the applied method.

References

[1] Zachariah M R and Egan G 2016 Mechanisms and microphysics of energy release pathways in nanoenergetic materials Energetic Nanomaterials: Synthesis, Characterization, and Application ed Zarko V E and Gromov A A (Amsterdam: Elsevier) chapter 4 pp 65–94

[2] Rashkovskii S A 2005 Combust., Explos. Shock Waves 41 35–46

[3] Rashkovskii S A and Savenkov G G 2013 Tech. Phys. 58 511–22