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The mechanism of formation of copper aluminide in the thermal explosion mode

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The mechanism of formation of copper aluminides in the thermal explosion mode was studied. A molded mixture of copper and aluminum powders was heated to the self-ignition temperature by the radiation of a tungsten heater. The phase transformations were detected by time-resolved X-ray diffraction (TRXRD). The kinetics of heat release due to the chemical reaction was studied by measuring the temperature of the sample. The macrokinetic stages of the process were revealed, and the apparent activation energy of each stage was estimated.

Key words: copper aluminides, thermal explosion, dynamics of phase formation, macrokinetics.

Copper aluminides possess higher stability and resistance toward corrosion than pure copper. They are characterized by high endurance, elasticity, and ductility. They are stable in air, including sea air, steam, and solutions of dilute acids. Copper aluminides are used for the production of gears, guide bushings, slip bearings, and armatures for work in fresh and seawater, a steam atmosphere, and others.

In the region of copper-rich alloys, the phase diagram is complicated and indicates many transformations undergone by the alloys in the solid state in the interval from the solidus temperature to 400 °C.[1] Copper aluminides are formed from the elements with heat release. The heats of formation of chemical compounds of aluminum with copper under standard conditions are[2] the following (kJ mol^{-1}): $AlCu_3$, 69; $AlCu_2$, 67; AlCu, 40; and Al_2Cu, 39. The reaction heat is sufficient to transform the synthesis of intermediates initiated in pre-heated mixtures of Cu and Al powders into a self-sustaining process.[3] Both the combustion and thermal explosion modes can be used to prepare copper aluminides.[4] It has previously[5] been shown that self-sustaining synthesis in the Cu—Al system is possible for aluminum concentration from 7 to 37 wt.% at an initial temperature of the sample equal to 300—500 °C. Combustion in the Cu—Al system occurs in the steady-state mode with a low rate of 0.1—0.8 cm s^{-1} depending on the conditions. The maximum temperature reaches 950 °C.

The phase composition and structure of products in the combustion and thermal explosion modes virtually coincide.[4,5] Monophase products were obtained for the compositions 2 Cu + Al and Cu + Al. Multiphase products were formed in other cases, but unreacted components were not observed. A large amount of

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unreacted copper was found only for the Cu + Al product containing 7 wt.% Al; this composition is the concentration limit of combustion.

The purpose of this work is the experimental study of the mechanism of the synthesis of copper aluminide in the thermal explosion mode.

Experimental

Two supplementing experimental procedures were used. The kinetics of heat release of the chemical reaction was studied by measuring the temperature of the sample over the whole process. The experimental installation is shown in Fig. 1. The sample was mounted on three molybdenum needles to reduce to minimum the conductive heat losses through the stand. The process was carried out in a vacuum of 10^{-3} Pa under the jar of a VUP-5M vacuum universal station. The sample was heated from the top with thermal radiation from a planar molybdenum thermal radiator. The metal screen that surrounds the sample from all sides had a hole equal to the sample diameter and arranged in such a way that the thermal flow from the heater fell only on the top face of the cylinder (not on the lateral sides). Therefore, the heating conditions were close to one-dimensional. Signals from thermocouples embedded in the top and bottom parts of the sample came through amplifiers to a computer. The frequency of temperature sampling depended on the rate of change in the signal from the thermocouple. During heating and cooling, the temperature was recorded once a second, and at the moment of exothermic reaction the frequency of temperature measuring reached 1000 per second. In addition, the process was recorded on a Panasonic NV-SD450 video tape recorder using a Panasonic WV-BL600 black-and-white camcorder attached to an OGME-PZ microscopic head, which made it possible to monitor a 15-fold amplified image on a display. The stoichiometric composition, initial density, and heating rate were varied in experiments, which allowed us to reduce to minimum temperature heterogeneities inside the sample.

The time-resolved X-ray diffraction (TRXRD) method described in detail previously[6] and modified according to the specific character of our experiments was used to determine the dynamics of change in the phase composition directly during experiments. The samples were placed in a resistance furnace and heated with a radiant thermal flow from molybdenum radiators. Experiments were carried out in helium (1 atm, linear heating rate 80—100 deg min^{-1}), and at the instant of thermal explosion the heating elements were switched off. During the whole process, including heating, thermal explosion, and cooling, X-ray diffraction patterns were continuously recorded into the computer memory. The recording frequency was varied from 1 to 5 spectra per second (the frequency increases at the moment of thermal explosion). The temperature in the center of the sample was monitored by a thermocouple.

The following compositions were studied: 3 Cu + Al, 2 Cu + Al, and Cu + Al. To prepare reaction mixtures, we used anodic copper powder (PMA) and the aluminum powder ASD-4 with a particle size of 44 and <20 μm, respectively. The samples, with a porosity of 25—12%, were prepared from the powdered mixtures by cold molding: for TRXRD, in the form of a parallelepiped of 13 × 8 × 18 mm and 15 g; and for thermometric measurements, as a cylinder with a diameter of 10 mm and a length of 5 mm. The temperature of the samples was monitored by tungsten—rhenium thermocouples with a junction thickness of 100 μm.

Starting and final samples were also studied by scanning electron microscopy and electron probe microanalysis on a JCXA-733 microanalyzer (JEOL) to determine their microstructure and chemical composition of structural components. X-ray analysis of the final samples was performed on a DRON-3 diffractometer.

Results and Discussion

The temperature change on two ends of the cylinder of the sample 2 Cu + Al with a density of 77.5% of the

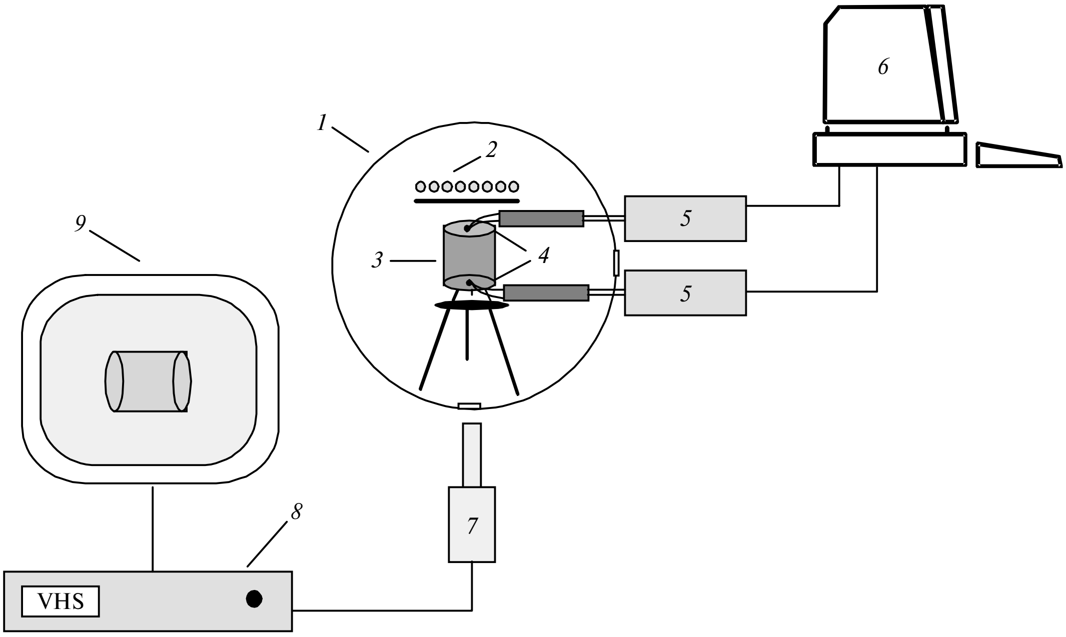

Fig. 1. Experimental installation for temperature measurement of the sample during thermal explosion: *1*, reaction chamber; *2*, heater; *3*, sample; *4*, thermocouples; *5*, amplifiers; *6*, computer; *7*, camcorder; *8*, video tape recorder; and *9*, TV monitor.

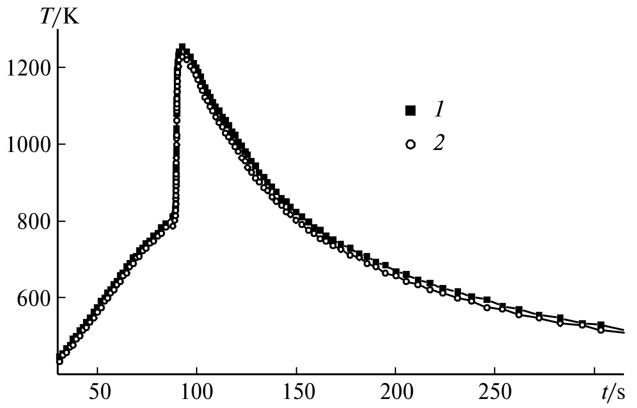

Fig. 2. The plot of the temperature of the 2 Cu + Al sample *vs.* time: top thermocouple (*1*) and bottom thermocouple (*2*).

theoretical value is shown in Fig. 2. It is seen that the temperature of the surface facing the heating element exceeds that of the opposite side by 5—30 K. The thermometric measurements and DTA of the samples showed that an intense heat release began near the eutectic temperature (821 K),[7] *i.e.*, below the melting point of aluminum (933 K).[7] The highest temperature reaches 1223 K, which corresponds to the value obtained previously.[5] The video recording of the high-density samples (80—70% of the theoretical value) shows that, when 673—800 K is achieved in the top part of the sample, melted droplets appear on the surface, descend as a wave, and are impregnated into the sample, leaving no trace. Then a uniform (over the sample volume) self-heating occurs without forming any hot spots or combustion fronts. For the samples with a density of 70—60% (of the theoretical value), the melt wave is not observed, but the thermal explosion is uniform over the whole sample volume. However, the difference between the temperatures of the top and bottom faces of the sample increases. For the samples with a density below 60%, a combustion wave is observed, which runs from the top to bottom layers, and the maximum difference in indications of the top and bottom thermocouples during the reaction reaches 100 K.

The study of the change in the temperature and its increase during thermal explosion (Fig. 3, *a*, *b*) showed that the main temperature increase occurred within 2 s, then its highest value was maintained for 4—5 s, and then the sample cools down. The maximum rate of the temperature increase is 700 deg s^{-1}, which is observed when the temperature of the system is ~1023 K. Then the rate of temperature increase decreases and reaches zero at the maximum temperature of the sample.

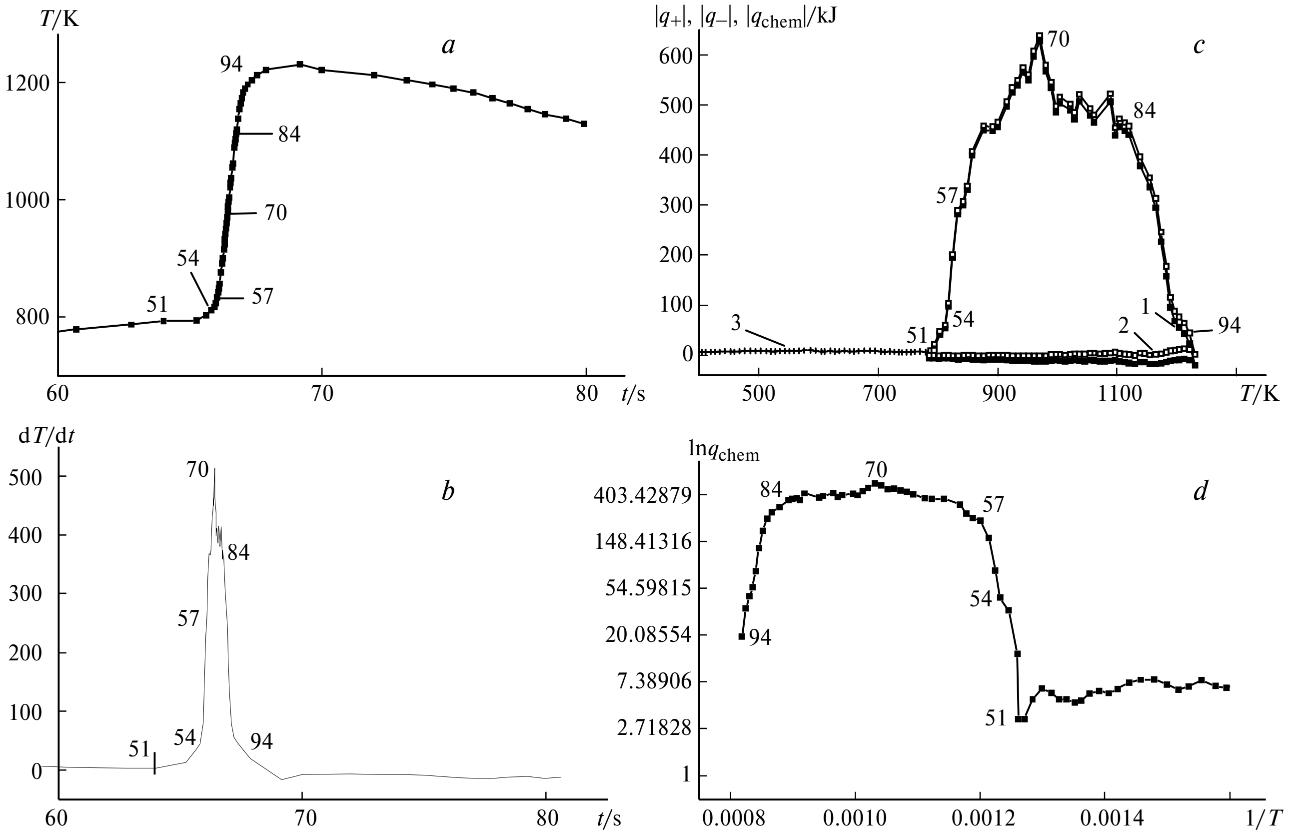

Fig. 3. Temperature profile of the reaction (*a*), heat release rate (*b*), thermal balance of the reaction (*c*) (*1*, heat release of the sample; *2*, chemical heat release taking into account heat losses; and *3*, heat obtained from the heater), and apparent activation energy of the reaction (*d*); numbers of some key experimental points are indicated.

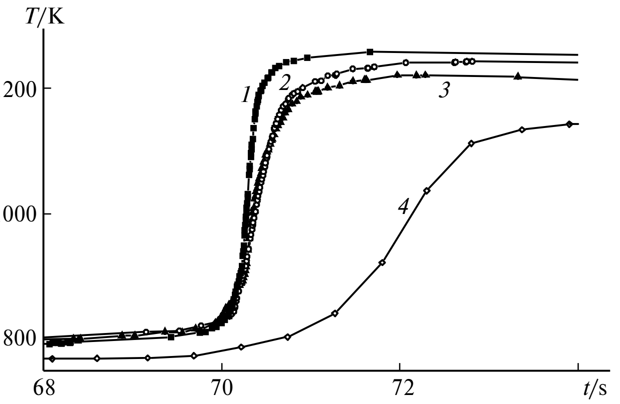

Fig. 4. Temperature profile of the reaction of the 2 Cu + Al samples during thermal explosion with a heating rate of 7 deg s^{-1} and initial densities of 75 (*1*), 62 (*2*), and 50% (*3*), as well as with a heating rate of 2 deg s^{-1} and an initial density of 75% (*4*).

The influence of the initial density and heating rate on the development of the thermal explosion is shown in Fig. 4. Curves *1*, *2*, and *3* correspond to samples 2 Cu + Al with the same heating rate of 7 deg s^{-1} and initial relative densities of 75, 62, and 50%, respectively. It is seen that with a decrease in the green density of the sample the maximum temperature of thermal explosion decreases, and the time of maximum temperature achievement increases. Curves *1* and *4* correspond to samples 2 Cu + Al with an initial density of 75% and heating rates of 7 and 2 deg s^{-1}, respectively. A decrease in the heating rate reduces the maximum temperature and extends the time of the exothermic reaction. At the same time, an increase in the heating rate to 15 deg s^{-1} does not further change the maximum temperature and reaction time.

The differences in the self-heating dynamics for the samples with different stoichiometric compositions are shown in Fig. 5. The temperature of the thermal explosion beginning is the same for all compositions. The maximum temperature of thermal explosion for 2 Cu + Al and 3 Cu + Al is close to the melting point of copper (1300 K), and for Cu + Al, it is lower than that (1050 K).

The changes in the phase composition and temperature of the sample 2 Cu + Al during the reaction (Fig. 6, *a*) found by TRXRD indicate that the thermal explosion begins at ~820 K, when aluminum melts, and the corresponding peak in the X-ray pattern decreases and then disappears. Then the intensity of the peak corresponding to copper decreases, and peaks of the new phase Al_4Cu_9 simultaneously appear. Then the formed new phase is ordered, and new peaks appear. All peaks become more sharp, *i.e.*, the intensity of the peaks increases, and their width decreases. Al_4Cu_9 is the main phase in the sample after the reaction.

The transformations of the phases during thermal explosion of the sample 3 Cu + Al are presented in Fig. 6, *b*. At first the phase Cu_3Al is formed, which, according to the phase diagram, upon cooling completely decomposes to Al_4Cu_9 and a copper-based solid solution. In our case, when the cooling occurs in an inert gas flow, the phase Cu_3Al decomposes incompletely, and the stronger the inert gas flow in the reaction chamber, the faster the cooling of the sample and the larger the amount of the Cu_3Al phase present in the final sample. When the reacted sample is heated to a temperature higher than that of decomposition of the

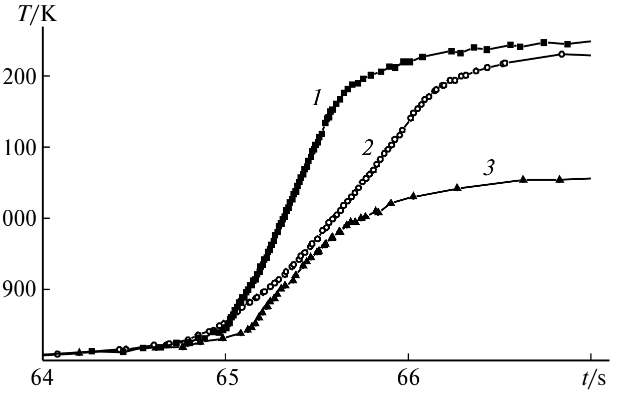

Fig. 5. Temperature profile of the reaction during thermal explosion for different samples: 2 Cu + Al (*1*), 3 Cu + Al (*2*), and Cu + Al (*3*).

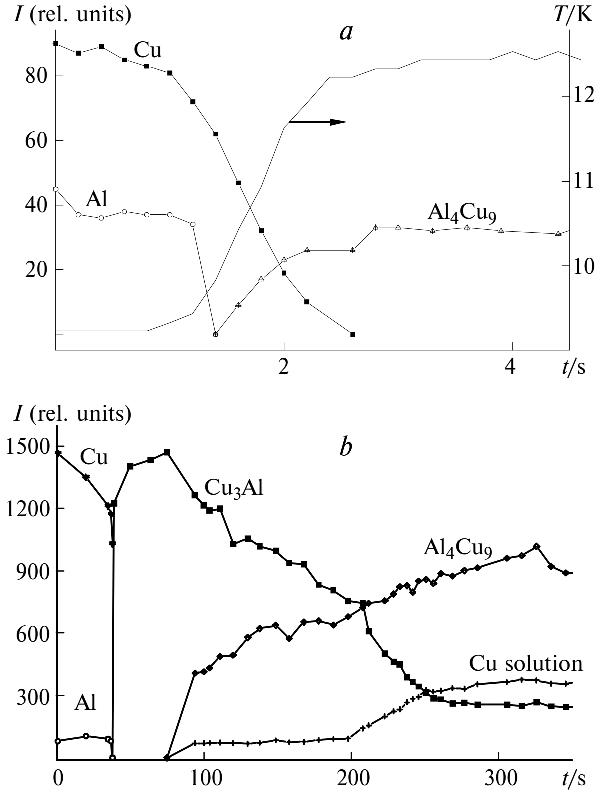

Fig. 6. Temperature change (solid line) and intensities of the peaks in the X-ray pattern during thermal explosion for the 2 Cu + Al (*a*) and 3 Cu + Al (*b*) samples.

Cu_3Al phase (838 K), the peaks of this phase again appear in the diffraction pattern, and Cu_3Al again decomposes on cooling according to the phase diagram. X-ray phase analysis of the final sample showed three phases, *viz.*, Cu_3Al, Al_4Cu_9, and a copper-based solid solution.

Using the detailed temperature profiles of the reaction (see Fig. 3, *a*), we can determine the kinetic stages of intermetallide formation. With this purpose, let us consider the thermal balance of the sample 2 Cu + Al during the whole process, including the exothermic reaction and cooling.

Neglecting the temperature distribution over the sample volume and knowing its weight (m, g), volume (V, m^3), and heat capacity (c, J kg^{-1} deg^{-1}), we estimate the change in the heat content of the body $c\rho V\mathrm{d}T/\mathrm{d}t$ (ρ is density), which includes the heat received by the body from the heater (q_+), the heat release rate during the chemical reaction (q_{chem}), and the heat losses to the environment (q_-)

$$c\rho V\mathrm{d}T/\mathrm{d}t = q_+ + q_{\mathrm{chem}} - q_-. \quad (1)$$

The reaction has already been completed in the cooling region ($q_{\mathrm{chem}} = 0$), and the heating source was switched off ($q_+ = 0$). Therefore, a change in the heat content of the body occurs due to the heat exchange between the body and environment

$$c\rho V\mathrm{d}T/\mathrm{d}t = q_-. \quad (2)$$

Since the sample is in a vacuum and has almost no contact with other bodies (mounted on needles), the body loses heat mainly due to emission from the surface

$$q_- = S\sigma\varepsilon(T^4 - T^4{}_{\mathrm{m}}), \quad (3)$$

where S (m^2) is the surface area of the sample, $\sigma = 5.67 \cdot 10^{-8}$ W mK^{-4} is the Stefan—Boltzmann constant, ε is the effective emissivity, T is the absolute temperature of the sample, and T_{m} is the environment temperature.

At low temperatures the effective emissivity ε can be estimated from formulas (2) and (3)

$$\varepsilon = (c\rho V\mathrm{d}T/\mathrm{d}t)/[\sigma S(T^4 - T^4{}_{\mathrm{m}})].$$

Then, extrapolating the effective emissivity values (ε) to high temperatures, we obtain its temperature function

$$\varepsilon = 1.2 - 6.05T, \quad (4)$$

where ε changes from 0.45 at $T = 1250$ K to 0.88 at $T = 500$ K.

The heat losses at high temperatures can be calculated by formula (3) using relation (4) and accepting $T_{\mathrm{m}} = 298$ K.

At the initial stage of heating, chemical reaction does not occur yet ($q_{\mathrm{chem}} = 0$), and the difference between the temperature of the body and the environment temperature is low. Therefore, heat losses can be neglected ($q_- \to 0$). Thus, the heat content of the body changes due to its heating from the radiation source.

$$c\rho V\mathrm{d}T/\mathrm{d}t = q_+$$

In the heat release region when the exothermic reaction starts, the heating source is switched off ($q_+ = 0$), and the heat content changes due to the chemical reaction (q_{chem}) and heat exchange between the body and environment (q_-). At the stage of chemical reaction, we obtain from formulas (1) and (4)

$$q_{\mathrm{chem}} = c\rho V\mathrm{d}T/\mathrm{d}t + S\sigma\varepsilon(T^4 - T^4{}_{\mathrm{m}}). \quad (5)$$

The components of the thermal balance are shown in Fig. 3, *c*. Curve *1* corresponds to the heat release in the sample obtained by formula (1), curve *2* corresponds to the chemical heat release calculated by formula (5) taking into account heat losses, and curve *3* corresponds to the heat obtained by the sample from the heater (q_+). It is seen that the considered heat losses introduce a slight correction.

Assume that the reaction (heat release) rate depends on the temperature according to the following law:

$$q_{\mathrm{chem}} = Q\rho k_0\exp(-E/RT), \quad (6)$$

where Q (J kg^{-1}) is the thermal effect of the reaction, k_0 (s^{-1}) is the pre-exponential factor, E (J mol^{-1}) is the activation energy, and $R = 8.3144$ J mol^{-1} K^{-1} is the universal gas constant. Then we can estimate the apparent activation energy of the process. Finding the logarithm of q_{chem}, we obtain

$$\ln(q_{\mathrm{chem}}) = \ln(Q\rho k_0) - E/(RT). \quad (7)$$

If expression (7) is plotted in the coordinates $\ln(q_{\mathrm{chem}})$ *vs.* $1/T$, the slope represents the $-E/R$ value (see Fig. 3, *d*).

The heat release process can conventionally be divided into three periods with different activation energies (see Fig. 3, *d*). The sharp heat release begins from the 51st point corresponding to 793 K and continues to the 57th point (833 K). The first period (from the 51st to 57th point) corresponds to the linear region in the plot, characterized by a high activation energy (~335 kJ mol^{-1}). The temperature increase during this period is small, and the heat release increases considerably from 10 to 250 deg s^{-1}. The second period (from the 57th to 84th point) corresponds to 1123 K. The main temperature increase occurs during this period, and the heat release rate is maximum. The activation energy is positive, although it becomes much lower (~0.3 kJ mol^{-1}). In the third region (from the 84th to 94th point, *viz.*, 1223 K) the reaction rate decreases despite the temperature increase.

A comparison of the obtained kinetic data with the TRXRD results allows us to conclude that the synthesis of copper aluminides in the thermal explosion mode includes four macrokinetic stages. The eutectic melt is formed at the first stage (793—833 K). Since this temperature is lower than the melting points of both reactants, the melt forms at the contact boundary due to the mutual diffusion of the solid reactants. The high activation energy of this stage also indicates a key role of solid state diffusion. When a sufficient amount of the melt is accumulated in the system, the second stage (833—1123 K) takes place: dissolution of solid copper in the melt with crystallization of the Cu_9Al_4 grains in the melt bulk. At this stage the main portion of the reactants is consumed, and the process is most intense after melting of aluminum. Since dissolution and diffusion in the liquid phase are weakly activated processes, the second stage is characterized by virtually zero activation energy. It should be emphasized that the solid product forms as precisely individual grains in the melt rather than a solid layer on the copper surface. Therefore, the reaction rate does not slow down as the solid phase Cu_9Al_4 forms. Finally, when the amount of the solid product increases and, correspondingly, the fraction of the melt decreases, the reaction slows down due to a decrease in the surface of the copper particles and screening of this surface with a layer of solid particles of the product. The reaction rate decreases despite a continuing temperature increase. This is the third macrokinetic stage of the process, occurring within the temperature interval from 1123 to 1223 K. The stage is completed when the dynamic equilibrium between the heat release and radiant heat losses is established, *i.e.*, on going to the fourth, final stage at which the reactions are completed, the crystal structure of the solid product is ordered, and the melt residues are crystallized. All these processes are accompanied by a comparatively weak heat release, which is sufficient, however, for compensation of the radiation heat losses. Therefore, the temperature is retained unchanged for 2—4 s. When the heat release cannot further compensate the heat losses, the sample begins to cool down. The described four macrokinetic stages were found for all compositions in the Cu + Al system.

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