

## HEAT AND MASS TRANSFER BETWEEN LOCAL COMBUSTION SITES IN METALLIC POWDER PREFORMS UNDER THERMAL-EXPLOSION CONDITIONS

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*Measurement of temperatures is made at different points in the volumes of exothermic cells and intervening spacings in model powder metallic preform mixtures during their combustion under thermal-explosion conditions. The presence of temperature gradients is found, as are regularities in their change in interrelation with specific features of migration of eutectics and melts formed in a porous metallic skeleton consolidated in a combustion wave.*

It is known that in sintering of powder metallic materials under volume-combustion (thermal-explosion) conditions high temperatures at which eutectics and melts are formed develop in local exothermic microvolumes [1]. Apparently, the spacings between them have a lower temperature. According to well-known laws of capillary heat and mass transfer [2], the temperature gradients in porous media are the main reason for migration of the liquid phase to the less heated parts. However, this aspect as applied to the mechanism of melt formation under thermal-explosion conditions is still inadequately studied [3]. This is due to the prevailing opinion that powder systems undergo thermal homogenization during combustion [4] due to instantaneous temperature equalization throughout the volume owing to the high thermal diffusivity of the metallic components of the mixture. The homogeneity theory of the thermal field is sufficiently fully elaborated [5], the heterogeneity theory is in its developmental stage.

However, neither of the two theories has been confirmed by temperature measurements in local volumes of the reactive cells or in intervening spacings because, first of all, of the small dimensions of their volumes, accurate attachment of microlocal temperature-sensitive elements on microsites of the structure-phase components of the powder material, and so on. In connection with these difficulties, we have conceived of the idea of modeling a compacted preform mixture having 100-fold increased microvolumes of the reactive zones and reactionless intervening spacings in the initial state. Then it will not be difficult to place thermal microcouple junctions on the investigated surfaces of exothermic cells and around them. Prior to modeling, we have been involved in research studies of specific features of the microstructure, and structure of reactive cells and intervening spacings that form the basis of the porous skeleton of a metallic powder material [6, 7].

In addition to the identity of the microstructure and its evolution in a combustion wave, in modeling mixtures with enlarged components we have also adopted equal specific powers of heat fluxes of exothermic cells, heat capacity, thermal conductivity of contacting volumes, and their ratio. For modeling, we employed the powder mixtures Ni+5 wt.% Al (below, "wt.%" is omitted), most often used in powder metallurgy for furnace sintering, and Ni+15Al, used in self-propagating high-temperature synthesis (SHS) of materials (SHS materials) to obtain powders and articles from the intermetallic compound Ni<sub>3</sub>Al.

According to investigations conducted previously, a reactive cell in the initial preform consisted of one or several aluminum particles in combination with a certain number of adjoining nickel particles. Their total volume represented a stoichiometric mixture from which the intermetallic compound Ni<sub>3</sub>Al (in our case) – the main SHS

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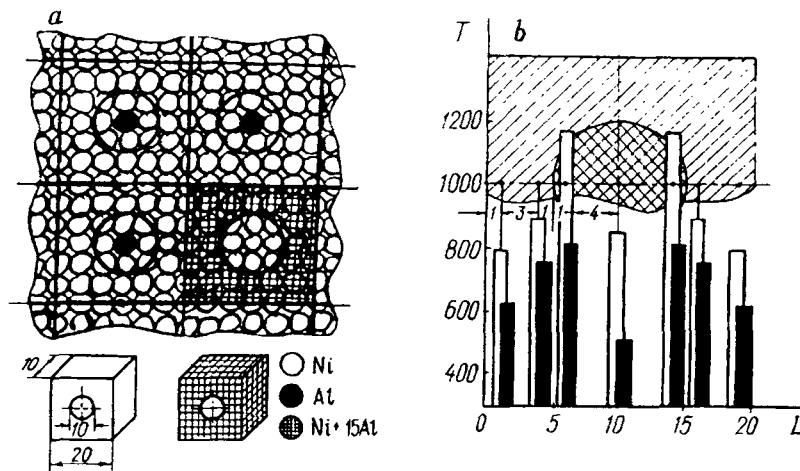


Fig. 1. Model scheme of a powder preform mixture: a) powder packing of mixtures of stoichiometric (hatched) and nonstoichiometric compositions; b) sites of temperature measurements in the model preform and a temperature histogram at the end of the combustion zone (light columns) and of the aftercombustion zone (dark columns).  $T$ , °C;  $L$ , mm.

product and a component of the model preform – was formed after combustion [1]. Actual and model mixtures were prepared from powders of the same grain size (40 ... 50  $\mu\text{m}$ ).

Figure 1a shows a model scheme of Ni+5Al (the unhatched squares) and Ni+15Al (the hatched square) mixtures with a reactionless cell, composed of nickel particles, located in the center of the square. It is quite obvious the regions shown by the squares will have the same temperature field for each mixture during combustion. We have prepared 20  $\times$  20  $\times$  10-mm rectangular prisms, 100-fold increased (see the lower part of Fig. 1a), as model preforms.

Preforming was accomplished in square molds in the following way: in the middle of the upper face of the lower punch a 10  $\times$  15-mm form-cylinder was placed, and the gap between the latter and the casing was filled with an alcohol-moistened mixture flush with the punch face, after which the punch was removed with a forceps. Then the cylindrical recess was charged with a cell mixture flush with the intermediate-spacing mixture, the upper square punch was installed, and bilateral preforming with a load of 4 ton/cm<sup>2</sup> was accomplished.

To obtain results of temperature measurements, the preform was brought in contact with the heating coil of an electric furnace, and on the upper face of the preform junctions of thermocouples (electrode diameters 0.1 mm) were attached at the required sites (denoted by dots in Fig. 1b). In heating the preform, their indications were recorded simultaneously on a paper tape of a printing recorder, with a recording frequency of 4 values per second. Due to the high frequency of recording, all points of the experimental curve merged together. The number of runs per record of a combustion wave was 5, which was quite sufficient for the  $\pm 5\%$  scatter in data at each point.

Figure 2 provides measurement results that illustrate the temperature distribution in reactive cells and between them. An analysis of the results shows that for the same time of measurement for all the points, their temperatures are never equal, and thermal equalization does not occur on the whole length of a combustion wave. The histogram in Fig. 1b allows the conclusion of the presence of considerable temperature gradients at each point both in the combustion zone (light columns) and at the end of the aftercombustion zone (dark columns). In Fig. 2 there are long isothermal sections on the curves, and temperature stabilization often occurs simultaneously at several points. This is indicative of the presence of steady heat and mass transfer conditions in the combustion wave that are associated with structure-phase changes in the powder system in accordance with the phase diagram.

The exothermicity of the processes lasts for 2000 ... 2200 sec under the experimental conditions, and then the temperature recording stabilizes at the level of heating by the electric coil to 560 ... 580 °C. The sole exception is the temperature variation at the center of the exothermic cell (see Fig. 2a, curve 2), which can be explained by

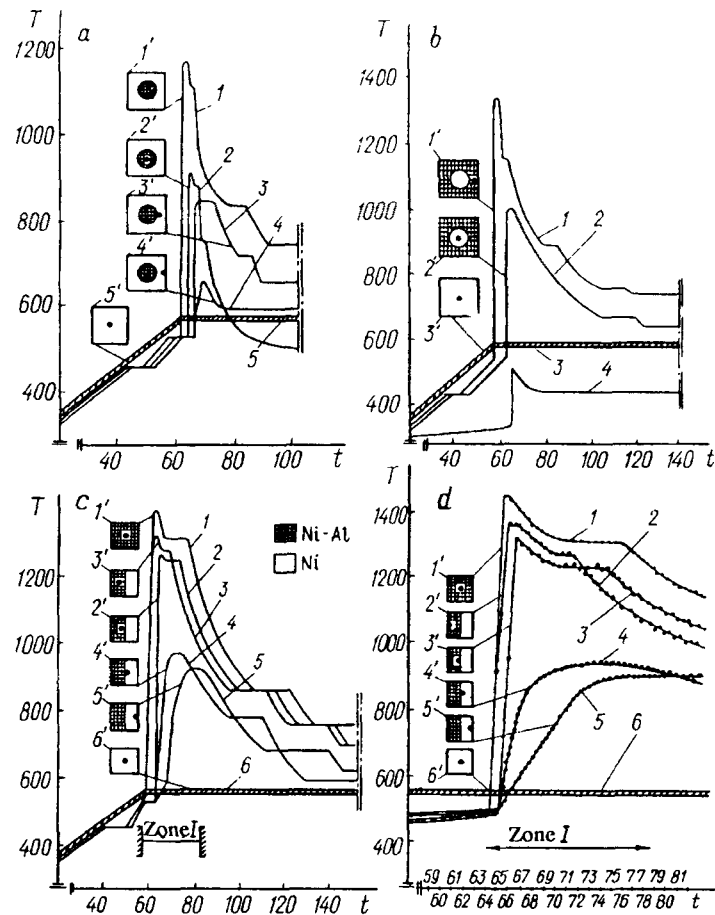


Fig. 2. Temperature profiles of combustion waves at different measurement points of model preforms: a) prepared from mixtures of nonstoichiometric compositions [1] at the point depicted on square 1'; 2) 2'; 3) 3'; 4) 4'; 5) 5'; b) from mixtures of stoichiometric compositions [1] at the point depicted on square 1'; 2) 2'; 3) 3'; 4) time variation of the air temperature at a point located a distance of 2 mm above the center of the specimen]; c) rectangular segments [1] at the point depicted on square 1'; 2) 2'; 3) 3'; 4) 4'; 5) 5'; 6) 6']; d) combustion wave in a narrow zone with an increased time scale (zone I in Fig. 2c; see designations of the curves in Fig. 2c).  $t$ , sec.

the hanging-up of the thermocouple junction after the formed eutectic migrated to the interspace and left a pore behind it. This mechanism of pore formation is described in [6, 7].

The special features described above were also observed in combustion of preforms prepared from stoichiometric mixtures, but at a higher heat release and fixed temperatures (see Fig. 2b). Recording 4 was made with a microthermocouple junction located 2 mm above the preform center. This gives grounds to expect that in combustion of exothermic preform mixtures, including ones of large dimensions, considerable heat losses to the environment will occur, which also favors development of temperature gradients between reactive cells.

In order to increase the exothermicity and provide the same conditions of heat and mass transfer between the reactive and reactionless cells, some samples were preformed as halved rectangles. The nature of the recording of the combustion wave for these preforms shows that the maximum temperatures at different points of measurement are markedly shifted in time. This is especially distinctly seen in Fig. 2c, d, where narrow combustion zone I is more extended in time. As is seen, at first the maximum temperatures appear at the interface, then at the edge of the reactive half of the preform, and finally at the edge of the reactionless half of the preform.

Thus, after ignition of a microlocal combustion site a thermal microwave is initiated that propagates from the boundary of a reactive cell into the depth of reactionless spacings. Apparently, heat is also transferred by a

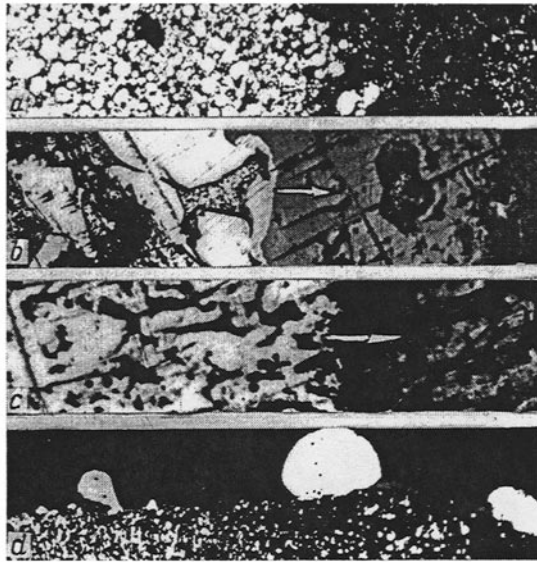


Fig. 3. Microstructure of the transition zone of a model preform: a) initial microstructure prior to heating,  $\times 50$ ; b) after heating at  $550^{\circ}\text{C}$  (the onset of Ni–Al eutectic formation),  $\times 500$ ; c) after heating at  $1400^{\circ}\text{C}$  (at the end of combustion),  $\times 100$ ; d) extrusion of droplets of the liquid phase on the "cold" end of the preform,  $\times 25$ .

liquid phase migrating through the phase boundary to less heated peripheral sections of the nickel matrix [3]. An increase of the temperature in the reactionless spacings can also be related to the appearance of new combustion sites at the places of contacts with the migrating liquid. Lower temperatures can be attributed to weakening of the reactivity of melt that has been saturated prior to this.

To explain the experimentally established facts of heat and mass transfer, we studied the evolution of the microstructure on each side of the interaction boundary. The dynamics of microstructure variation was observed directly in combustion under a PMT-3 hardness-gauge microscope on a section specimen of the upper face of a preform, the lower end of which was heated by an electric coil of a microfurnace placed on the microscope stage of the hardness gauge with reliable heat insulation. Visual observation was combined with recording of the combustion wave, which allowed unambiguous interpretation of the temperature and structure changes.

Figure 3a shows the initial microstructure of a preform that represents an impression of a polished punch. This method of thin-section preparation prevents deformation-caused distortions of the microstructure. In heating of preforms to  $420\text{--}450^{\circ}\text{C}$ , the aluminum particles became round after their saturation with a low-temperature eutectic [8, 9], which was accompanied by temperature stabilization (the first plateau in the recording). The second isothermal straight line immediately prior to ignition is related to aluminum melting and eutectic formation, and the latter instantaneously disappears from the microscope field of view after ignition since it dissipates in capillary pores and largely separates out on the less heated face of the sample under the microscope. This makes subsequent observation of microstructure changes difficult. The latter were judged from microsections of specimens quenched after a stay in different zones of the combustion wave.

Figure 3b shows the microstructure of the transition boundary at the moment of appearance of the Ni–Al eutectic and the beginning of its migration to the porous nickel interspace. The subsequent increase in the volume of the liquid phase in the reactive cell and its extensive transfer through the interface can be judged from Fig. 3c. Here, the impression is created that the migration at this stage proceeds under pressure, with formation of longitudinal channels for displacement perpendicular to the interface. Evidently, this occurs owing to excess pressure due to a difference in the surface tension of the melts in capillaries one end of which is adjacent to the high-temperature zone of the exothermic cell, and the other to the less heated intervening medium. This is confirmed by thermal extrusion of the melt in the form of droplets photographed at the less heated face of the model preform (see Fig. 3d).

TABLE 1. Calculated Data for Temperature Determination in the Spacings Between Local Combustion Sites

Line No.	$r_1, \mu\text{m}$	$r_2, \mu\text{m}$	$r, \mu\text{m}$	$T_1, ^\circ\text{C}$	$T_{\text{ig}}, ^\circ\text{C}$	$T_{\text{ig}} - T_1, ^\circ\text{C}$	$r_1 r_2 / (r_2 - r_1)$	$1/r_1 - 1/r$	$T_r, ^\circ\text{C}$
1	5000	10,000	8000	1180	580	-600	10,000	0.00007	760
2	5000	10,000	6000	1180	580	-600	10,000	0.00003	1000
3	50	100	60	1180	580	-600	100	0.007	760

In practice, this a mechanism of liquid-phase displacement plays a very positive role in consolidation of gradient powder SHS materials [10] with alternating reactive and reactionless layers, where the strength of the material depends on the quality of capillary "soldering" of transition joints by the migrating eutectic. However, in sintering of powder metallic materials from exothermic mixtures the development of temperature gradients in the case of one-sided heating from the furnace bottom by an electric coil can exert an unfavorable effect, namely, the melt undergoes one-sided displacement and accumulation at less heated end faces, nonuniform shrinkage, sweating-out, and so on [3].

To justify the modeling method described above it is necessary to prove:

- a) identity of the structure-phase processes of consolidation of powder contacts under combustion conditions, especially in the transition zone between reactive cells and spacings in actual and modeled preforms;
- b) satisfactory agreement of temperature gradients in spacings between reactive cells for different dimensions for them.

The first point can be proved by comparing results of research studies of structure-phase processes in actual powder mixtures [6-10] and the aforementioned data on specific features of microstructure evolution (Fig. 3) in a combustion wave of a model macroheterogeneous preform mixture: the same order of disposition of like phases on each side of the interface is seen (interaction products in eutectic migration to reactionless, less heated spacings, etc.). This can be explained by the identical physical state of contacts formed at different compaction forces and temperature regimes of heat treatment, at which the sequence and essence of the processes remain the same in an initial microlocal combustion cell consisting of a cluster of nickel particles around a single aluminum particle and in an initial model macrocell, i.e., a local combustion site consisting of a conglomerate of numerous aluminum and nickel particles with their ratio being constant. Here, the size of the aluminum particles (the main component) is not of crucial importance since prior to ignition aggregated nickel particles are already impregnated by melted particles (one or many) of aluminum, while the spacings of the nickel skeleton are not impregnated. Naturally, some macrokinetic characteristics of combustion (the amount of heat in the cell, ignition temperature, combustion rate, etc.) change, but only quantitatively. The main thermophysical characteristics (the specific heat flow, thermal conductivity, dimension ratios of volumes, temperature of heating to ignition, maximum combustion temperatures of the same mixture in the cell) remain unchanged, which determines the identity of heat and mass transfer processes.

An answer to the second question concerning the influence of the dimensions of the micro- or macrolocal combustion sites and their spacings can be provided by an analysis of results obtained from the formula [11]

$$T_r = T_1 + (T_{\text{ig}} - T_1) \frac{r_1 r_2}{r_2 - r_1} \left( \frac{1}{r_1} - \frac{1}{r} \right), \quad (1)$$

where  $r_1$  is the radius of a combustion site;  $r_2$  is the distance from the center of a combustion site to the middle of the spacing between neighboring sites;  $r$  is the distance from the center of a combustion site to any point on the straight line connecting the centers of neighboring combustion sites;  $T_r$  is the temperature at the point  $r$ ;  $T_1$  is the temperature at the boundary of passage from a local combustion site to a spacing (on the basis of the obtained results in Fig. 1b,  $T_1 = 1180^\circ\text{C}$ );  $T_{\text{ig}}$  is the temperature of additional heating of the preform to ignition (in our case and according to [1, p. 59],  $T_{\text{ig}} = 580^\circ\text{C}$ ).

The data necessary for the calculations and the results obtained are given in Table I. The first line contains the calculated  $T_r$  at an intermediate point (as applied to Fig. 1b), and the second line, at a point near the boundary. A comparison of the calculated and experimental values reveals sufficiently good agreement of them. Judging from the results of the third line, where the dimensions of the combustion sites and the spacings are decreased by two orders of magnitude, the temperature remains the same, which is indicative of the validity of the principles of modeling of macroheterogeneous powder mixtures for investigation of heat and mass transfer under thermal-explosion conditions.

It should be noted that formula (1) is derived for steady heat and mass transfer conditions. However from the experiments described in the present work and in [6-10] it is established that the temperature profiles of the combustion wave possess long horizontal sections. This points to the existence of consolidation and heat and mass transfer processes under steady thermal conditions. Therefore, use of formula (1) in our case is justified, especially in view of the fact that theoretical computational models of a heterogeneous solid flame are not available.

Based on the experimental results obtained, it can be stated that:

1) in the course of consolidation of metallic powder preforms under volume-combustion conditions in a thermal-explosion regime a temperature gradient develops between local exothermic cells with a tendency of temperatures to decrease toward the center of the spacings between the cells; the magnitude of the gradient depends on the concentration of the chemically interacting components;

2) thermal heterogeneity in the volume of the burning preform exists along the entire combustion wave;

3) the presence of temperature gradients in SHS consolidation initiates displacement of the eutectics and melts produced by combustion to less heated spacings between reactive cells, which favors hardening of powder materials and homogenization of their composition.

## NOTATION

$L$ , distance to the right from the left-hand edge of the model preform to the temperature measurement points (Fig. 1b), mm;  $T$ , temperature plotted along the ordinate-axis (Figs. 1 and 2), °C;  $T_r$ , temperature at the point  $r$ , °C;  $T_1$ , temperature at the boundary of passage from a local combustion site to a spacing, °C;  $T_{ig}$ , temperature of additional heating of the preform to its ignition, °C;  $r$ , distance from the center of a combustion site to any point lying on the segment of the straight line connecting neighboring combustion sites.

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