CONDITIONS OF PROPAGATION OF THE SHS REACTION FRONT IN NANOLAYERED FOILS IN CONTACT WITH HEAT-CONDUCTING MATERIAL

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The problem of propagation of the gas-free combustion (SHS reaction) front in nanolayered foils in thermal contact with the mating surfaces is considered. It is shown that dependence of the rate of propagation of the combustion front on the intensity of heat removal is of a threshold nature: there are critical values of the intensity of heat removal at which the combustion conditions in the nanolayered foil–heat-conducting material system are suppressed.

Keywords: *welding and brazing, multilayer foils, heat-conducting materials, mating surfaces, self-propagating high-temperature synthesis reaction, heat removal, threshold thickness, analytical estimation*

Materials in which the self-propagating high-temperature synthesis (SHS) reaction may occur between their components are regarded as good candidates for production of permanent joints by the welding or brazing methods [1–3]. Of special interest are multilayer foils (MF) consisting of layers based on intermetallic-forming components, in which under certain conditions the SHS reaction may take place with a high intensity of heat release. As thickness of the MF layers is decreased to the nanoscale level, the rate of propagation of the SHS reaction may amount to several metres per second, and the intensity of heat release may grow to 1–2 kW/cm^2. Location of such highly reactive foils between the mating surfaces with the SHS reaction initiated in them allows activation of the diffusion processes within the joining zone due to the heat release or melting of a filler metal during brazing. This makes it possible to form permanent joints in materials without their melting. Models allowing for the processes of diffusion interaction of components in MF and heat release under the conditions where there is no heat removal to the environment were developed to predict the rate of propagation of the SHS reaction front, temperature at the front and intensity of heat release [4–8].

To predict characteristics of occurrence of the SHS reaction under the conditions where MFs are in contact with the mating surfaces, it is necessary to allow for the reverse effect of heat removal on the reaction [9, 10]. In this case we might expect non-linearity in behaviour of the system and, in particular, existence of the combustion/extinction phase transition with a change of the heat removal parameters. Apparently, heating in the front at a very intensive heat removal may be insufficient for further occurrence of the reaction. So, the question is whether decrease in the rate of occurrence of the SHS reaction with increase in heat removal is a gradual process or it stops upon reaching some threshold intensity of heat removal.

Studies [5–7] offer a simple model of occurrence of SHS in MF. A foil consisted of M alternating layers of components with multilayer spacing $4l$ (l is half of thickness of a layer of one component), allowing for a layer Δy_0 thick that reacted before the beginning of SHS. Along with a numerical solution of the model for one- and two-stage reactions, an analytical formula for estimation of the rate of movement of the front at the absence of external heat removal was offered and tested:

$$V = \sqrt{\frac{2a_{foil}^2 D_0 \Delta g T_0 (k_B T_f + Q)}{c(1-c)4l^2 - \Delta y_0^2 Q^2 (T_f - T_0)} \exp\left(-\frac{Q}{k_B T_f}\right)}, \qquad (1)$$

where c is the mean concentration of a new phase with diffusion characteristics D_0 and Q, and thermodynamic formation stimulus per atom, Δg; a_{foil}^2 is the thermal diffusivity of the foil; k_B is the Boltzmann constant; T_0 is the initial temperature of the foil; T_f is the maximal temperature at the front, which is determined by phase formation energy Δg multiplied by foil efficiency factor $f = 1 - \Delta y_0/2l$:

$$3k_B(T_f - T_0) = f\Delta g. \qquad (2)$$

In study [6], this approach was specified with allowance for the final rate of relaxation of vacancies in metal foils, which substantially decreased predictable rates of the SHS reaction.

The present study considers occurrence of the SHS reaction in MF compressed between two heat-conducting plates (e.g. plates of brazing filler metal, which should be heated or melted by means of SHS). Then the heat removal may either inhibit the reaction or fully suppress it. As seen from formula (1), rate V of the reaction is determined, in the first turn, by front temperature T_f. Apparently, the heat removal should decrease heating of the foil. In this case, the degree of the decrease is determined by the rate: the slower the reaction, the longer is the time of propagation of the front through a given point, the more heat is removed during the front propagation time, and the higher is the temperature drop. Therefore, there is a positive feedback between the decrease in rate and temperature drop, and this feedback may lead to escape from the steady-state condition, i.e. to extinction. To quantitatively estimate it, it is necessary to determine dependence of the degree of decrease in temperature on the rate of the SHS reaction. Consider the analytical estimation, and then specify it by means of numerical solution of the problem of unsteady heat transfer.

Analytical estimation. Density of the flow of heat removal, $j_Q^{\perp}$ from the MF surface (Figure 1) is determined by characteristics of a contact material:

$$j_Q^{\perp} = -\kappa_p \frac{\partial T}{\partial y} \eta, \qquad (3)$$

where κ_p is the coefficient of thermal conductivity of contact plates; and η is the dimensionless coefficient of efficiency of the contact, which depends on the roughness of the contact surface and is defined by the efficient contact area to total area ratio ($0 < \eta \leq 1$).

To allow for the effect of heat removal on occurrence of the SHS reaction, it is enough to determine the heat flow at a given point only within time τ_f of propagation of the front through this point. By using standard solution of the one-dimensional problem, we can assume that the transverse temperature gradient that determines the heat removal has the Gaussian profile:

$$\frac{\partial T}{\partial y} \sim -\frac{T_c - T_0}{\sqrt{\pi a_{foil}^2 t}} e^{-y^2/(4a_{foil}^2 t)}, \qquad (4)$$

where T_c is the temperature at the contact.

One of the approximations, i.e. formula (4), is made at a constant temperature on the surface. In our case this temperature changes with propagation of the front. Therefore, it is necessary to check the derived formulae by the numerical solution, where equation (4) is not used.

If temperature T_c at the contact during front propagation time τ_f increases from T_0 to the maximal value of T_f, the mean transverse temperature gradient can be estimated by replacing $T_c - T_0$ with $(T_f - T_0)/2$ and time t with τ_f in (4).

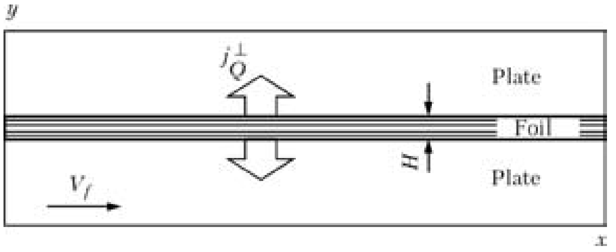

Figure 1. Schematic of heat removal in foil–plate system

Then we allow for the heat removed and, hence, for a change in temperature during the front propagation time (not after), as it is this fact that determines the intensity of the reaction, whereas cooling of the foil after the SHS reaction has practically no effect on the front propagation rate. Moreover, width of the front can be estimated in much the same way as width of the diffusion zone in diffusion, $L_f = \sqrt{a_{foil}^2 \tau_f}$. At the same time, front width is $L_f = V_f \tau_f$. Based on this fact, the mean transverse temperature gradient within the region of the SHS front can be described as $\frac{\partial T}{\partial y} \sim \sim \frac{T_f - T_0}{2\sqrt{\pi}} \frac{1}{V_f \tau_f}$. Therefore, the heat flow density is inversely proportional to the rate of the front and its propagation time:

$$j_Q^{\perp} = \frac{\kappa_p \eta}{2\sqrt{\pi}} (T_f - T_0) \frac{1}{V_f \tau_f}. \qquad (5)$$

Then the total amount of the heat removed through unit of the foil surface area is inversely proportional to the rate

$$j_Q^{\perp} \tau_f = \frac{\kappa_p \eta}{2\sqrt{\pi}} (T_f - T_0) \frac{1}{V_f}.$$

Allowing for a double-sided contact of the foil with the contact plates, heat removal from surface area S_0 of the foil is defined as $j_Q^{\perp} \tau_f 2S_0$. Assume that the heat is removed uniformly from each atom in a given cross section of the foil. This assumption is valid only for a sufficiently thin foil, if the time of levelling of the temperature across the section is much shorter than the time of propagation of the front through this section: $(H/2)^2/a^2 << a^2/V_f^2$, i.e. $H << 2a^2/V_f \approx \approx 2L_f$. Simply speaking, thickness of the foil should be markedly smaller than width of the SHS front. Otherwise, it is necessary to calculate the temperature profile along the section of the foil. Area S_0 of the foil with thickness $H = M4l$ comprises $S_0 H/\Omega$ atoms (Ω is the atomic volume). Hence, the analytical estimation of heat removal per foil atom is

$$q_{an} = \frac{j_Q^{\perp} \tau_f 2}{H/\Omega} = \frac{\kappa_p \eta}{2\sqrt{\pi}} \frac{2\Omega}{H} (T_f - T_0) \frac{1}{V_f}. \qquad (6)$$

Allowance for the heat removal leads to modification of formula (2):

$$3k_B(T_f - T_0) = f\Delta g - \frac{\kappa_p \eta}{2\sqrt{\pi}} \frac{2\Omega}{H} (T_f - T_0) \frac{1}{V_f}.$$

As a result, we obtain the required dependence of the front temperature as a function of the front propagation rate:

$$T_f = T_0 + \frac{f\Delta g}{3k_B(1 + U/V_f)}, \qquad (7)$$

where $U = \frac{1}{3k_B}\frac{\kappa_p\eta}{2\sqrt{\pi}}\frac{2\Omega}{H}$ is the parameter which, allowing for the Dulong–Petit law, can be interpreted as a rate of heat removal (ratio of foil thickness $H/2$ to characteristic time of its cooling, $(H/2)^2/a_p^2$):

$$U = \frac{\eta}{\sqrt{\pi}}\frac{a_p^2}{H}, \tag{8}$$

where a_p^2 is the thermal diffusivity of the plate. Parameter U is the intensity of heat removal (in particular, $U = 0$ at its absence).

Numerical calculation of heat removal. To check and specify analytical estimation (7), the two-dimensional boundary problem was numerically solved to determine thermal conductivity in a rectangular plate adjoining the foil (Figure 2, *a*) at a preset temperature profile of SHS (Figure 2, *b*), which was used as a boundary condition at the foil–plate contact:

$$T(x,\ y = 0,\ t) = \begin{cases} T_f, & x < V_f t, \\ T_0 + (T_f - T_0)\exp\left(\dfrac{x - V_f t}{L_f}\right), & V_f t < x. \end{cases}$$

The boundary conditions at the remaining three sides of the region are trivial: $T(x,\ y = P_y,\ t) = T_0$, $\frac{\partial T}{\partial x}(x = 0,\ y,\ t) = 0$, $\frac{\partial T}{\partial x}(x = P_x,\ y,\ t) = 0$.

Heat flows released by the foil to the plate through the contact zone, $P_y = 0|P_y = 1$, up to the moment of reaching the maximal value of temperature T_f were summed up for each mesh point:

$$q_{num} = \kappa_p\eta\frac{\Omega}{H/2}\int\limits_{\frac{x}{V_f}-\frac{2L_f}{V_f}}^{\frac{x}{V_f}} -\frac{\partial T(x,\ y)}{\partial y}\Big|_{y=0} dt'.$$

The values of the heat flow were averaged by points of the contact zone.

As shown by numerical calculations, the rough analytical estimation (6) was proved to be accurate: $q_{an}/q_{num} = 1.023$ (at $\eta = 1$, $H = 20$ μm, $T_0 = 300$ K, $T_f = 2000$ K and thermal conductivity for tin $\kappa_p = 65.7$ J/(m·s·K)).

Therefore, the analytical, inversely proportional dependence of heat removal on the front propagation rate is correct, and formulae (7) and (8) can be used for further analysis of the combustion and extinction conditions.

Self-consistent calculation of temperature and rate of the front. Formulae (1) and (7) realise the positive relationship between the front rate and decrease in temperature as a result of heat removal. By substituting formula (8) to (1), we obtain the transcendental equation for the SHS front rate as a function of characteristic heat removal rate U and foil efficiency f.

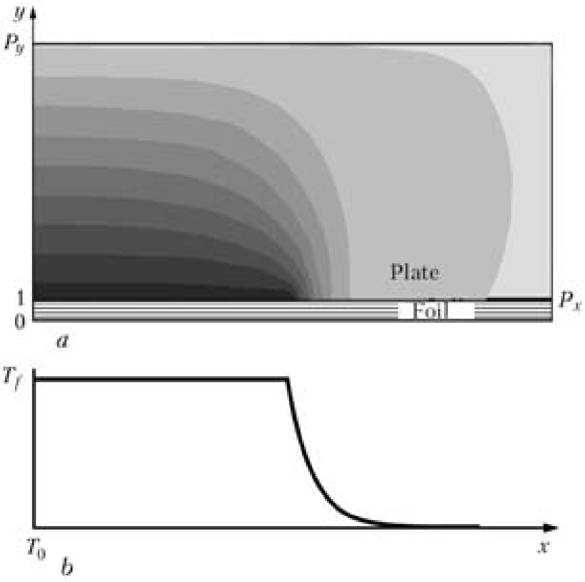

Figure 2. Propagation of heat in plate adjoining the foil surface as a result of propagation of SHS wave (*a*) with temperature profile (*b*)

As is evident from formula (8), the U value can be controlled by changing the contact efficiency and foil thickness. Figure 3, *a* and *b*, shows the maximal temperature and rate of the SHS reaction front depending on this or that parameter, the rest of characteristics of the system being constant. Both dependences have a jump corresponding to some critical value of the intensity of heat removal, U_{cr}, at which solution of the system of equations (1) and (7) transfers in a jump to $V_f = 0$ and $T_f = T_0$, i.e. the SHS reaction is probable at $U < U_{cr}$, and it is extinguished at $U > U_{cr}$.

Another factor of no small importance, which determines switching of the combustion/extinction conditions, is multilayer spacing $4l$. As shown in studies [4–6], the front propagation rate at the absence of heat removal is of a non-monotonous character at a change in the multilayer spacing (Figure 3, *c*): Δy_0 has a substantial effect at a small spacing, and diffusion activity of phase formation falls at a big spacing. Both factors decrease heating in the SHS reaction and, hence, the probability of its occurrence.

Moreover, it was experimentally proved that the combustion reaction may occur in low-reactivity multilayer foils at their insignificant heating before initiation of the reaction [11]. Increase of the ambient temperature leads to exponential growth of the diffusion coefficient and, hence, the rate of heat release to maintain the SHS condition.

Therefore, the probability of the SHS reaction in MF, which is in thermal contact with the mating surfaces, is determined by the following factors:

1) roughness or pressure on the contact of foils with plates — the lower the pressure, the worse is the thermal contact, the higher is the thermal resistance at the contact, and the closer is the heat removal coefficient to zero (see Figure 3, *a*);

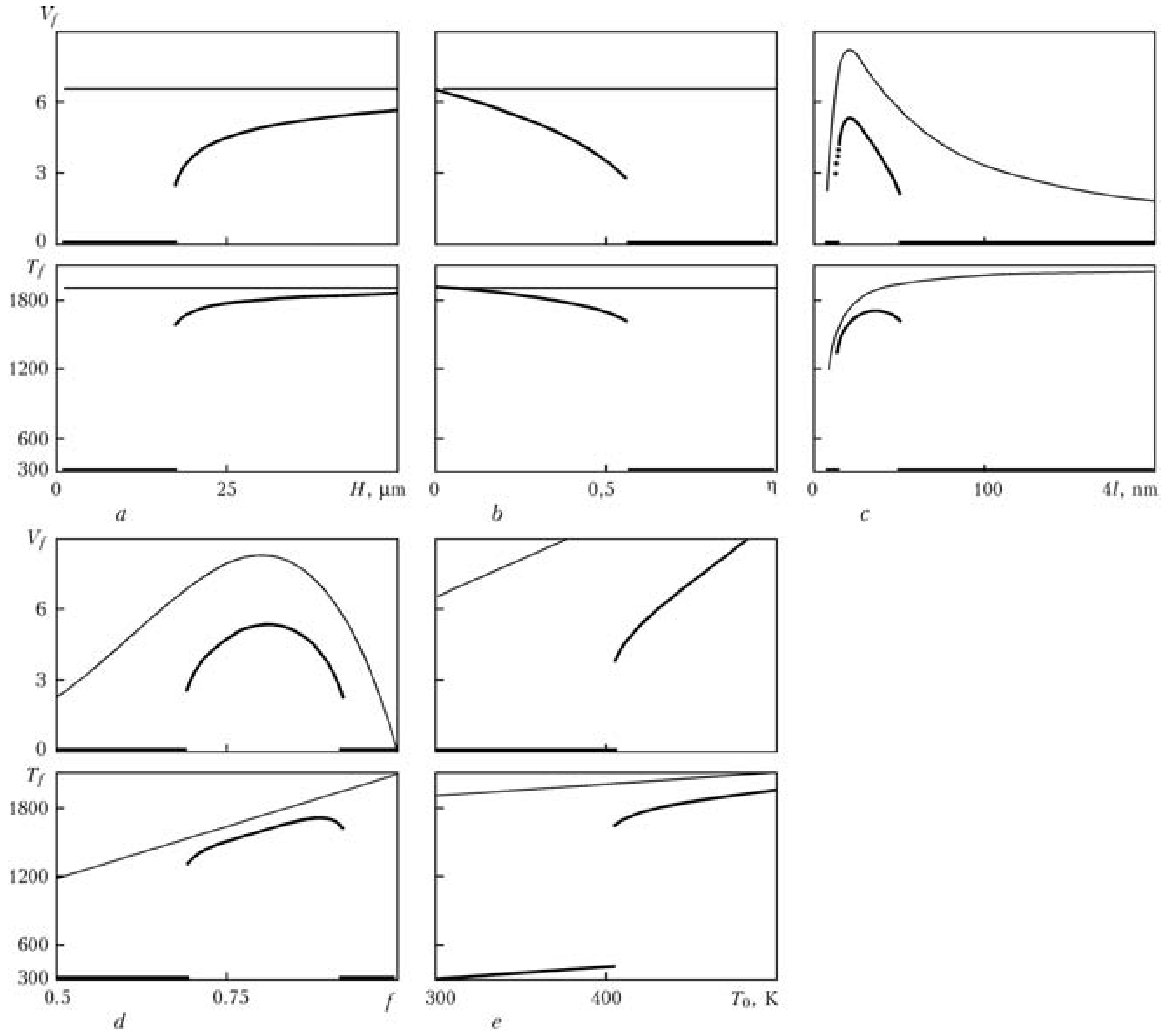

Figure 3. Dependence of rate V_f and maximal front temperature T_f on foil thickness H (*a*), contact efficiency coefficient η (*b*), multilayer spacing $4l$ (*c*), foil efficiency coefficient f (*d*) and initial temperature T_0 (*e*): thin and thick lines — SHS conditions without and with heat removal, respectively ($c = 0.5$, $D_0^* = 1.5\cdot10^{-5}$, $Q = 1.7$ eV, $\Delta g = 0.46$ eV, $a^2_{foil} = 7.42\cdot10^{-5}$ m^2/s, $a_p^2 = 4\cdot10^{-5}$ m^2/s, $\Delta y_0 = 2$ nm, $4l = 40$ nm, $f = 0.9$, $H = 20$ μm, $T_0 = 300$ K, $\eta = 0.5$); for Figure 3, *e*, $\eta = 1$

2) foil thickness H — the thicker the foil at a constant spacing, the more efficient is the heating, and the more difficult is suppression of the reaction (Figure 3, *b*);

3) spacing $4l$ and efficiency f of a MF multilayer — non-monotonous dependence $V_f(4l)$ is sensitive to heat removal at the multilayers that are too thin (f is low, as interlayer Δy_0 is always present), and at the thick layers (close to the systems of micron sizes) the extinction is absent only in a certain range of values of multilayer spacing $4l$ (Figure 3, *c*) or foil efficiency f (see Figure 3, *d*);

4) ambient temperature T_0 — the higher the initial temperature of the foil–plate system, the more efficient is the reaction diffusion, and the more difficult is suppression of the reaction (see Figure 3, *e*).

Whereas the third and fourth factors have an indirect effect on the heat removal by determining an insufficient local heating at a low rate of propagation of the SHS wave, the first two factors directly determine the intensity of the heat removal (8).

It seems reasonable to re-write the ratio for the critical set of parameters, at which the combustion is probable, in the form of dependence $H(\eta, U)$. Then, the rest of the parameters being fixed, it is possible to add the critical value of thickness

$$H_{cr} = \frac{\eta}{\sqrt{\pi}} \frac{a_p^2}{U_{cr}}. \qquad (9)$$

Let us call parameter H_{cr}, above which the steady-state SHS condition is possible, the combustion threshold. Then condition $H > H_{cr}$ can be regarded as a combustion criterion at the fixed value of η. At the same time, at a constant thickness of the foil the combustion criterion can be the threshold value of $\eta_{cr} = \frac{\sqrt{\pi}H}{a_p^2} U_{cr}$ (the reaction occurs at $\eta < \eta_{cr}$).

Dependence of critical foil thickness on phase formation energy and diffusion activation energy. As the rate of the SHS front is determined primarily by reaction stimulus Δg and reaction activation energy Q, the extinction criterion depends on the same parameters. Solution of the system of equations (1) and (7) at different values of Δg, Q and η, and at fixed values of $4l$ and f, showed that dependence $H_{cr}(\Delta g, Q, \eta)$ can be well approximated by exponential function

$$H_{cr}(\Delta g, Q, \eta) = \eta H_0(\Delta g) \exp\left(\frac{Q}{Q^*(\Delta g)}\right), \qquad (10)$$

where $Q^*(\Delta g) \approx b_Q \Delta g + Q_0$, $H_0(\Delta g) \approx b_H \ln(\Delta g / Q_0)$, coefficients b_Q and b_H depend on multilayer spacing $4l$ and foil efficiency f (the exact type of the dependences will be considered in a separate study).

CONCLUSIONS

1. It is shown that allowance for heat removal from the SHS reaction front propagating in a nanolayered foil in thermal contact with an environment may lead to its extinction under certain conditions.

2. Combustion is possible if the characteristic rate of heat removal determined by equation (8) is higher than the threshold value, which depends primarily on the diffusion activation energy, thermodynamic stimulus of intermetallic formation and temperature of the environment.

3. Extinction of the SHS reaction in the MF–heat-conducting material system can be avoided by increasing thickness of the foil, deteriorating thermal contact between the elements of the system, increasing temperature and reactivity of the foil (by selecting thickness of the layers which provides a higher rate of propagation of the SHS reaction front, and by decreasing thickness of intermetallic at interfaces between the layers).

4. Analytical approximation (10) of the threshold thickness is suggested for the combustion condition with regard to the activation energy and thermodynamic stimulus of the reaction.

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