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THE GAS-FREE BURNING OF A MIXTURE OF METAL POWDERS

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As is known, the process of gas-free burning consists in the fact that when particles of various powders interact, a great quantity of heat is released, while the reaction products are liquids or solids. In this sense it is of significant interest to study the gas-free burning of a mixture of powders of various metals having complex phase diagrams. The reactions developing in the solid phase or in the presence of the liquid phase lead, on the boundary of the heterogeneous particles, to the formation of chemical compounds. Since the reaction surface in a disperse system is large, while the occurring phases have a high heat of formation and a specific volume that differs from the matrix, with simultaneous formations of large quantities of the new phase the compressed mixture of metal powders is strongly heated and increases in volume.

This article is devoted to a study of the gas-free burning of mixtures of Ni-Al and Cu-Al powders, the kinetics of reaction diffusion in these mixtures, and the process of the increase in volume of the briquets due to the formation of new phases.

To study the nature of phases in powder mixtures we performed x-ray microspectral, x-ray structural, metallographic, and microdurometric analyses. The nature and sequence of the phases forming on the interface of nickel and aluminum particles after vacuum annealing in the 530-590°C temperature range are as follows: Ni—$NiAl$—Ni_2Al_3—$NiAl_3$—Al. The phases Ni_2Al_3 and Ni_3Al, or only Ni_2Al_3, form in the bimetal Ni-Al.

The following phases form in the bimetal and the mixture of copper and aluminum powders on the interface of the various particles after heating in the 440-530°C temperature range: Al—α-solid solution of copper in aluminum—$CuAl_2$—$CuAl$—Cu_2Al—$\varkappa$-solid solution of aluminum in copper—Cu.

The table gives the results of measurement of the layer of product formed around the aluminum particles in mixtures of Ni—Al and Cu—Al powders and on the interface in the corresponding bimetals. The growth rate of the individual phases and the common region is determined by the diffusion of atoms through the product layer, and the change in layer thickness is subject to the law

$$x^n = K_1(t - t_0)f(R), \tag{1}$$

where x is layer thickness; t is time; t_0 is the latent period; R is the particle radius; K_1 and n are constants.

The kinetics of the growth of the individual phases and the entire region in a mixture of copper and aluminum particles and Cu—Al and Ni—Al diffusion vapors are described by a parabolic law ($n = 2$) which, for a mixture of spherical powders, is a particular case of the more general equation

$$x^2\left(1 - \frac{2}{3} \cdot \frac{x}{R}\right) = K_2\tau. \tag{2}$$

In accordance with this, the degree of conversion (α) is subject to the Yander equation [1]

$$1 + (1 - \alpha)^{2/3} - 2(1 - \alpha)^{1/3} = K_3(t - t_0), \tag{3}$$

where

$$\alpha = 1 - \left(\frac{R - x}{R}\right)^3 .$$

Cu—Al	Phases	$K \cdot 10^{11}$, cm²/s at T (°C)				t_0, min at T (°C)			E, kcal/mole
		440	470	500	530	470	500	530	
Bimetal	CuAl+Cu_2Al	—	12,3	31,3	77,2	135	60	15	36
	$CuAl_2$	—	1,6	3,2	5,8	135	60	15	25
	Common region	—	22,9	55,7	126,4	135	60	15	34
Mixture of powders	CuAl+Cu_2Al	0,97	4,4	21	56,8	Latent period very slight			53
	$CuAl_2$	1,1	3,3	9	25,6				39
	Common region	4,1	15,2	59,7	160				48

Ni—Al	Phases	At T (°C)										E, kcal/mole
		500	530	560	590	620	500	530	560	590	620	
Bimetal	Common region	—	—	0,8	1,4	3,2	—	—	150	144	57	38
Mixture of powders	Common region	0,04	0,06	0,09	0,17	0,33	19	5,5	5,4	5,3	5	24

The kinetics of the growth of the region in a mixture of nickel and aluminum powders are subject to the law $x^3 = K_4(t - t_0)f(R)$, while the degree of conversion is described by the equation

$$x + 3(1 - x)^{2/3} - 3(1 - x)^{1/3} = K_5 t/R^3. \qquad (4)$$

By comparison with diffusion in a bimetal, reaction diffusion in a powder mixture has essential features caused by the developed specific surface, the high distortions of the crystal lattice of the reacting metals and the forming phases, and also by the presence of pores and microcracks. In a mixture of copper and aluminum powders the layer of phases CuAl + Cu_2Al grows more slowly, while the layer of the $CuAl_2$ phase grows much more rapidly than in the bimetal Cu—Al. In a mixture of nickel and aluminum powders the coefficients of diffusion in the Ni_2Al_3 and NiAl phases are much higher than in the bimetal. The growth rate of the common region of the reaction product in mixtures of Ni—Al and Cu—Al powders is higher, while the latent periods are several times lower than in bimetals. As a result, even in the early stages of the process a continuous spherical layer of product forms which uniformly contracts into the particle.

A decrease in particle size leads to an increase in phase growth rate, and it is impossible to trace the kinetics of reaction diffusion. It is also impossible to study the initial stages of the process. In these cases the growth of the layer is probably subject to another kinetic equation. For diffusion in a bimetal this has been obtained analytically [2] and has the form

$$x = K_6 t. \tag{5}$$

The linear law becomes parabolic at various stages of the process, when the concentration on the surface is still far from saturated.

With passage through the melting point of the eutectic, on the boundary of the heterogeneous particles the liquid phase forms which easily flows over the briquet, covering the powder particles with a thin layer. The kinetics of reaction diffusion in this case should apparently be subject to equation (5).

The formation of chemical compounds and solid solutions in mixtures of Ni–Al and Cu–Al powders on the interface of the heterogeneous particles leads to heating of the briquets. The heat release increases with increasing dispersion of the powders and the aluminum content in the mixture.

To study the influence of aluminum concentration on the nature of the heating we linearly heated (5°/min) a briquetted mixture of Ni–Al powders (η_0 = 20%, dispersion <50 μ) at a pressure of 10^{-2}–10^{-3} mm Hg. With an increase in aluminum concentration (C) from 1.5 to 20%, the self-ignition point of the mixture drops from 560 to 520°C, while the magnitude of the effect ($\Delta T = T_{\text{макс}} - T_0$) increases approximately by the linear law $\Delta T = a(c - b)$, where $a = 66$ and $b = 1$ - const. With a low aluminum concentration (to 2%) the thermal effect develops due to the formation of chemical compounds in the solid phase, and its value is low (30-100°C). With a high aluminum content in the mixture (2.5-15%) the thermal effect is high (ΔT = 280-600°C). At first, heating occurs due to the reaction in the solid phase, but basically it is associated with the appearance and spread of the liquid phase which forms at temperature above the eutectic (640°C) and reacts with the surface of the solid particles. With aluminum concentrations of 20-30% the specimen explodes.

Let us examine the problem of the thermal heating of a reaction system due to the formation of a chemical compound. Let substance A, having the shape of spheres with varying radii R_i of which $\overline{R}$ is the most probable, be surrounded by a layer of substance B, and on the interface the chemical reaction $mA + nB = A_mB_n + q$ develops; q is the thermal effect of the reaction. Let us assume that its rate is subject to the Arrhenius equation. The quantity of heat released in a volume of mixture per unit time $Q_1 = q(dM/dt)$, where M is the mass of the forming phase, while the heat removed by the surface of the system is Q_2. Their difference goes toward heating of the system:

$$Q_1-Q_2=cm\cdot\frac{\partial T}{\partial t}, \qquad (5')$$

where c is the specific heat, and m is the mass.

Let us consider that the volume of the phase is greater than that of particle A (this is confirmed experimentally). Therefore we must consider that both the inner and outer phase boundaries are moveable. To take this into consideration let us assume that no cavities form in particles A. Then $\gamma m_A = m_B$; $\gamma d_A v_A = d_B v_B$, and the mass of the phase formed on an individual particle of A $m = m_A + m_B = d_A v_A(1 + \gamma)$, where $\gamma = nA_B/mA_A$; m_A and m_B, d_A and d_B, v_A and v_B, and A_A and A_B are the masses, densities, volumes, and atomic weights of the substances entering into the reaction. Since conversion ceases when $x_1 = R$, we can write

$$m(R)=d_A v_A(R)(1+\gamma)\Theta(R, x),$$

where

$$\Theta(R, x_1)=\begin{cases}1 \text{ when } x_1 \leqslant R\\ 0 \text{ when } x_1 > R.\end{cases}$$

The sum of all elementary masses forming on spheres A having various dimensions

$$M = \sum n_i m_i = N \sum \frac{n_i m_i}{N} = N \int_{R_{\text{мин}}}^{R_{\text{макс}}} m(R) f(m)\, dm,$$

where n_i is the number of particles with mass m_i; $f(m)$ is the distribution density function, which we can give if we know $m = \varphi(R)$ and $f(R) = \frac{1}{\sigma_0 \sqrt{2\pi}} e^{-\frac{(R-\overline{R})^2}{2\sigma_0^2}}$ (normal distribution of particles by sizes).

According to the theorem of statistics

$$\overline{m} = \frac{M}{N} = \int_{-\infty}^{+\infty} \varphi(R) f(R)\, dR;$$

$$M = N \int_{-\infty}^{\infty} d_A v_A(R)(1+\gamma)\Theta(R, x) f(R)\, dR = \tag{6}$$

$$= \frac{4\pi N d_A (1+\gamma)}{3\sigma_0 \sqrt{2\pi}} \int_{-\infty}^{+\infty} [R^3 - (R-x_1)^3]\Theta(R_1 x_1) e^{-\frac{(R-\overline{R})^2}{2\sigma_0^2}}\, dR,$$

where x_1 is the thickness of the phase layer.

As shown above, $x_1 = K\sqrt{t}$ if diffusion is the limiting stage of the process, and $x = Kt$ if the reaction is limiting. By substituting the expression for x into (6) and finding dM/dt, we can determine Q_1.

The value $Q_2 = Q' + Q''$, where $Q' = \alpha S(T - T_0)$ is the removal of heat due to thermal conductivity and $Q'' = \sigma(T^4 - T_0^4)A\varepsilon_1\varepsilon_2$ is the heat removal by radiation (α is the heat-transfer coefficient; S is the geometric surface of the system; T is the system temperature; T_0 is the ambient temperature; ε_1 and ε_2 are the radiation coefficients; σ is the Stefan-Boltzmann constant).

Substituting the expressions for Q_1 and Q_2 into equation (5') we get

$$\frac{dT}{dt} = \beta \cdot \frac{dM}{dt} - \xi(T^4 - T_0^4) - \chi(T - T_0), \tag{7}$$

where

$$\beta = \frac{4\pi q N d_A (1+\gamma)}{3\sigma_0 \sqrt{2\pi}\, cm};$$

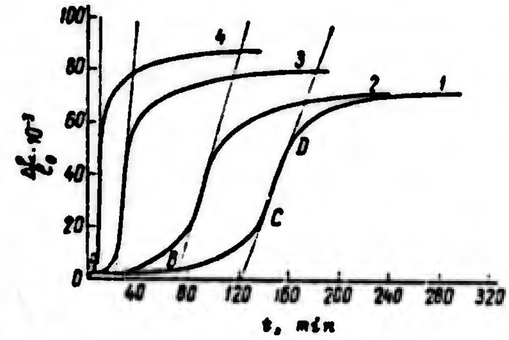
$$\xi = \frac{S_r c r_1 \varepsilon_2}{cm};$$

$$\chi = \frac{a_0 S_r}{cm};$$

$$I = \int_{-\infty}^{+\infty} [R^3-(R-x)^3]\, e^{-\frac{(R-\bar{R})^2}{2\sigma_0^2}}\, \Theta(R, x_1)\, dR.$$

Equation (7) was solved by numerical integration on an EVM-20 for the case when the growth of the layer is described by the equation $x^2 = Kt$ (mixture of Cu–Al powders). The approximate solution agrees well with the experiment data. It was not possible to use equation (7) to describe the thermal effects developing on the interface *solid phase-liquid* because of the lack of kinetic parameters.

Reaction diffusion in a powder mixture leads to a great increase in volume of the briquets. The results obtained during the vacuum isothermal heating of Ni–Al mixtures ($D_{Ni} < 63$ μ; $D_{Al} = 63$-100 μ; $\eta_0 = 25\%$) and Cu–Al and Fe-Al mixtures in the 510-580°C temperature range show that the change in dimensions of the briquets with time is described by an S-shaped curve (see the figure). The growth of the briquets involves processes of atomic and reaction diffusion which lead to the formation, around the particles, of an aluminum region of solid solutions and chemical compounds with a specific volume different from that of the matrix. The formation and growth of these phases are accompanied by the occurrence, in the contact region, of a crystallization pressure which can be so high that the briquet splits and disintegrates.



Dilatometric curves for briquets made from a mixture of Ni-Al powders: 1 – 510°C; 2 – 530°C; 3 – 560°C; 4 – 580°C.

If we examine a porous body as an aggregate of regions of radius L in which the stresses are balanced, the field of elastic stresses caused by the crystallization pressure can break down due to splitting of the briquet along the intraparticle contact surfaces. Then the particles obtain relative freedom of motion, which leads to a further increase in the volume of each elastically-stressed region and of the entire specimen as a whole. Here it is assumed that breakdown of the field of elastic stresses occurs by laws of branched chain reactions with interacting chains. Therefore, to describe the processes of an increase in volume and the splitting of briquets we can use the concepts developed by N. N. Semenov [3].

The equation describing the change in volume of the specimen has the form

$$\Delta V(t) = \int_0^t \Delta V(x) \left(\frac{dn}{dt}\right)_x dx,$$

where $\Delta V = {}^4/_3 [(L_0 + \Delta L(t))^3 - L_0^3]$ is the change in volume of the elastically-stressed region during unloading; $\frac{dn}{dt} = f_1 n - f_2 n - gn + N(t)$ is the number of regions unloaded in 1 s; f_1 is the probability of branching in 1 s; f_2 is the probability of chain termination in 1 s caused by migration of the particles that does not lead to an increase in volume of the specimen; $g = g_0 n$ is the probability of chain separation in 1 s caused by interlacing of the chains; $N(t) = N_0 \varphi \cdot \frac{dG}{dt}$ is the number of elastically-stressed regions which can be established in 1 s due to a growth of the phase layer; N_0 is the number of particles of component A; G is the degree of conversion; φ is a coefficient.

If we set $f_1 - f_2 = f$, the time dependence of the change in volume can be obtained in the form

$$\Delta V(t) \cong \overline{\Delta v}\, \frac{2\overline{N}\left(e^{t\sqrt{\Delta}} - 1\right)}{(f + \sqrt{\Delta}) - (f - \sqrt{\Delta})e^{t\sqrt{\Delta}}},$$

where $\Delta V(t) \approx \overline{\Delta v}$ and $N(t) \approx \overline{N}$, while $\Delta = f^2 + 4g_0\overline{N} > 0$.

It is easy to show that the time dependence of changes in volume are of an S-shaped nature.

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