Formation of a transition layer between the particle and the matrix in the presence of non-ideal contact

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Abstract. Experimental study of the reaction sintering process of CuO-Al powders revealed the problem of poor wetting of particles by the melt. The effect of poor wettability can be both incompatibility of components in the mixture and the presence or appearance of intermediate oxide or other layers at the interface. In mathematical modelling of the process of diffusion zone formation between an oxide particle and aluminium melt under sintering conditions, consideration of these factors leads to problems with non-ideal diffusion contact. For a spherical particle such a problem is solved numerically. Different variants of possible diffusant distribution in the vicinity of the interface are demonstrated.
Keywords: sintering, diffusion, non-ideal contact.

1. Introduction

Powder metallurgy methods, including liquid-phase sintering, are actively used to synthesize new materials with unique properties. Thus, when using a mixture of powders, in which aluminum-thermal reactions leading to the formation of hardening particles are possible, due to the significant heat release in the reactions, all processes occur in the liquid phase. However, the surface features of the initial particles and the phenomenon of wettability can affect the synthesis result. This also applies to the CuO-Al.

Copper oxide can be used to fabricate Al and/or copper-based nanocomposites in situ [1–3]. The reaction product is Al_2O_3 alumina particles, which act as a reinforcing phase. The reduced copper dissolves in the Al lattice or forms intermetallides, which can improve the mechanical properties of the final product. In [4], an Al-Cu based composite reinforced with α-Al_2O_3 nanoparticles was synthesized by performing an Al-10CuO liquid-solid reaction followed by a hot extrusion process. The Al_2O_3/Al-Cu composite after extrusion was found to have a heterogeneous structure consisting of alternately distributed zones rich in Al_2O_3 particles and zones poor in Al_2O_3 particles. The authors distinguish Al, Al_2Cu and Al_2O_3 in the composition of the composite.

Note that at present the exact mechanism of the termite reaction Al+CuO has not been established, despite the fact that it is one of the most energetically efficient oxygen-containing termites [5]. The interaction in this mixture may be hindered, for example, by the presence of an oxide shell on aluminum particles [6]. The reactions may be inhibited due to slow diffusion through aluminum oxide, which controls reactions of this type.

Different authors note that incompleteness of metallothermal reactions and complex composition of the reinforcing phase, which is not predicted in advance, may be due to imperfect particle shape, inhomogeneous mixing of powders, the presence of impurities (which is due to the way the samples were prepared for the experiment), the presence of oxide film on the surface of aluminum particles; poor wetting of particles by the melt, etc. The problem of poor wettability of particles with melt, known for the synthesis methods of Al_2O_3/Al-Cu Ex-situ composites remains in the method of synthesis of In-situ from Al and CuO powders. All these phenomena are in one way or another related to the interfaces, the important role of which between CuO and Al/Al_2O_3 reactants is emphasized in [7]. The interfaces largely determine the physical and mechanical properties of the obtained composites.

The aim of the research is to study the peculiarities of sintering of CuO-Al powder mixture. This paper presents the results of a preliminary experiment demonstrating the existence of the

problem of poor wettability in the CuO-Al system and the presence of non-ideal contacts between the particles and the melt. A model demonstrating the role of these effects in the formation of diffusion zones in the vicinity of interfaces is proposed.

2. Experiment

Commercial powders of aluminum (PA-4, < 100 μm) and copper oxide (PMA, < 125–160 μm) were used in the experiment. The ratio of powders was chosen in such a way that the amounts of interacting components were sufficient to realize the reduction reactions existing in these systems for possible reactions of intermetallide synthesis from free metal elements. Al-CuO according to the total reaction:

$$7Al + 6CuO = 2Al_2O_3 + 3AlCu_2. \tag{1}$$

In this case, the amount of initial components for the selected composition in weight percentages of 54 weight % Al + 46 weight % CuO.

From the prepared mixtures, cylindrical specimens with a diameter of 10 mm and a height of 10–15 mm were pressed. The pressing or molding of the samples was carried out on a hydraulic press. Pressing was carried out using a mold with movable upper and lower punch.

Two variants of thermal treatment were used: vacuum sintering at a fixed temperature due to infrared radiation from tungsten heaters [8] and a mode of constant heating from a fixed temperature heater to initiate a possible thermal explosion [9].

At the temperature (650 °C) under sintering conditions, no appreciable reaction processes with formation of reduction products were recorded, although the transition of copper (II) oxide to Cu2O oxide was revealed. Increasing the temperature up to 800 °C had a significant effect on the reactivity. As a result, the samples not only did not retain their shape, but also fragmented in the form of droplets (there was spattering of the powder material of pressings due to the intensive formation of the liquid phase (aluminum and eutectic). The violent reaction was accompanied by the dispersion of the sample. This was apparently facilitated by the destruction of the oxide film on aluminum due to local mechanical stresses, which was accompanied by the release of aluminum and rapid reactions with high heat generation.

Fig. 1 shows a sintered sample, which shows protruding drops of metal (aluminum), on the basis of which the assumption of poor wettability was made.

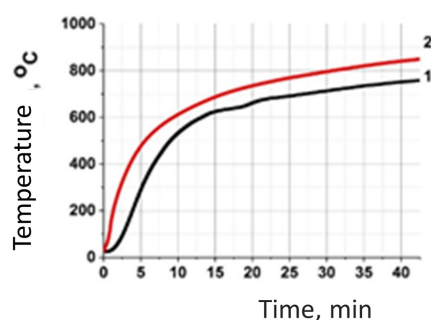Fig. 1. Photograph of pressed Al+CuO system after sintering.

Fig. 2. Thermogram of heating of pressed Al+CuO mixture.

In the second case, the temperature curve typical for thermal explosion could not be obtained (Fig. 2). The furnace temperature was 900 °C, and the pressing was heated in a fireclay cup. The reaction onset time, determined from the kink in the temperature curve, was 1085 s, the corresponding temperature was 642 °C. The reactions do not proceed to completion in either case. Presumably, the reactions are inhibited due to poor wettability of the copper oxide by the aluminum melt. PCA data show the presence of CuO, Cu_2O and Al in the products.

3. Mathematical model

Suppose that the particle has a spherical shape. The process of interaction between the particle and the matrix begins after melting of aluminum, which surrounds the particle. In the Al-CuO system, atoms of three varieties can diffuse in principle, and reactions with the formation of new phases begin when some concentration values are reached. Up to these values, the interface between the particle and the aluminum melt can be considered stationary. The formation of transition zones between the particles and the environment can be associated with the migration of impurities, which are quite numerous in these systems due to the way of sample preparation. Impurities can be introduced specifically to provide conditions for the formation of contacts. To study the process of formation of the transition layer between the particle and the matrix, let us consider an idealized situation. Two situations are possible – mutual diffusion of aluminum and copper until some critical conditions are reached or diffusion of impurity from the matrix region until the desired contact is formed. In either case, to solve the problem of contact formation we need only one concentration, which in the matrix region we will denote as Y_m and in the particle region as Y_p. These are the same element (diffusant), but in different regions.

As a result, we come to the conjugate problem of diffusion in the spherical coordinate system (Fig. 3). This problem includes the diffusion equation written for the particle region and the matrix region:

$$\frac{\partial Y_p}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_p \frac{\partial Y_p}{\partial r},\right), \; r \leq R_0 \tag{1}$$

$$\frac{\partial Y_m}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_m \frac{\partial Y_m}{\partial r}\right), \; R_0 < r \leq R_1, \tag{2}$$

where R_0 – effective radius of particles; R_1 – radius of the matrix area per particle; D_p, D_m – diffusion coefficients of the mobile element (for example, aluminum or specially introduced impurity) in particles and matrix, depending on temperature according to the Arrhenius law (however, at a fixed temperature the coefficients may depend only on composition, which is taken into account when writing the equations); Y_p – concentration of diffusant in the particle; Y_m – in the matrix.
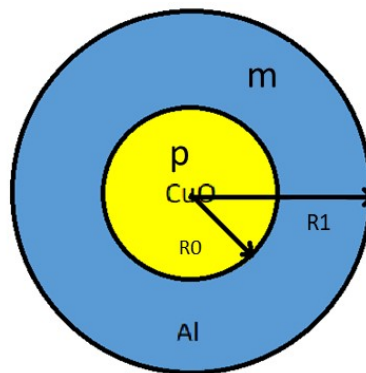

Fig. 3. Explanation of the problem statement (p – particle area; m – matrix area per one particle; R_0 – effective radius of the particle).

The symmetry condition is satisfied in the center of the particle:

$$r = 0 : D_p \frac{\partial Y_p}{\partial r} = 0. \tag{3}$$

Boundary conditions at the outer boundary, i.e. at $r = R_1$, have the form:

$$r = R_1 : \ D_m \frac{\partial Y_m}{\partial r} = 0 . \tag{4}$$

The boundary conditions at $R = R_0$ depend on the type of the system under study.

The problem of poor wetting of particles by the melt, which is associated with a change in the kinetics of transition layer formation, is reflected in the boundary condition as follows:

$$r = R_0 : D_p \frac{\partial Y_p}{\partial r} = D_m \frac{\partial Y_m}{\partial r} ; \tag{5}$$

$$Y_m = Y_{m0} \Phi(t) , \tag{6}$$

where $\Phi(t)$ – is given function reflecting the dynamics of contact change and satisfying to following conditions. At the initial time moment, a contact absents, $Y_m = 0$. Then contact should gradually appear and at $t \rightarrow \infty$ we shall obtain $Y_m = Y_{m0}$.

In the case of ideal contact condition (6) takes the form

$$Y_p = Y_m \gamma_0 . \tag{7}$$

where γ_0 - const, depending on the ratio of mobility of diffusants in different areas.

This condition is satisfied, for example, by the function

$$Y_m = Y_{m0} efrc \left(\frac{\gamma}{2 D_s \sqrt{t}} \right) ,$$

where D_S – surface diffusion coefficient; γ – surface tension coefficient. After the concentration reaches the value Y_{m0}, new phases may appear, and this problem ceases to be correct. It is necessary to formulate new boundary conditions that take into account the growth of new phases [10].

The condition at the boundary in the presence of diffusion resistance is formulated as follows

$$Y_p - Y_m = -\frac{\delta}{D_S} D_p \frac{\partial Y_p}{\partial r} . \tag{8}$$

At the initial moment of the time, the concentration distribution is given by:

$$Y_p = 0 ; \ Y_m = 1 . \tag{9}$$

This problem was solved numerically by an implicit difference scheme of the second order of approximation in spatial steps and the first order in time; the double sweep method was used. The results presented below demonstrate a qualitative difference in the concentration distribution for different situations.

Fig. 4 shows that the concentration distribution in the vicinity of the interface in the case of ideal contact between the particle and the matrix is typical for diffusion problems. The gap in concentrations, if it exists, is preserved for any moment of time, which is specially emphasised in Fig. 4b.

In case of poor wettability there is no contact at the initial moment of time, but it gradually appears until the solubility limit is reached (Fig. 5a). Then new phases may appear, which requires a special formulation of the problem.

In the case of non-ideal contact due to diffusion resistance (Fig. 5b), we also observe changes in the diffusant concentration distribution. A gap is observed which decreases with time. It becomes practically equal to zero with time.
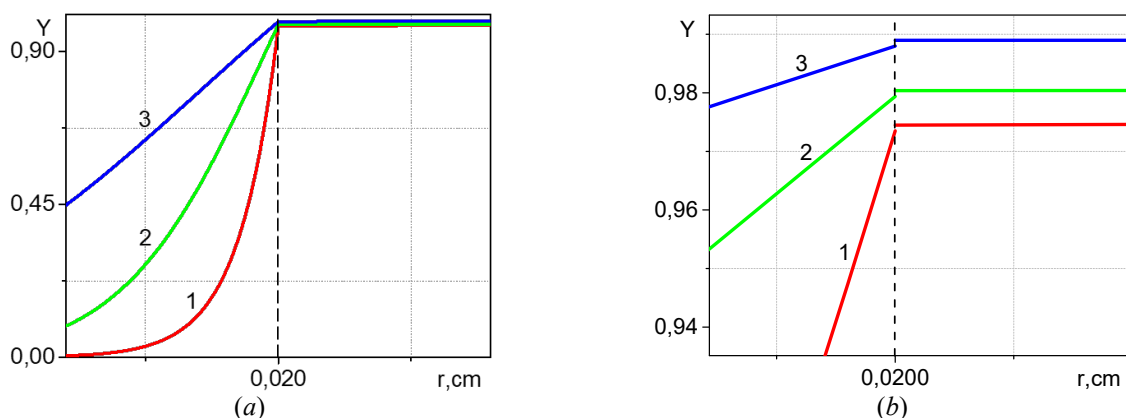

Fig. 4. Diffusant concentration distribution in the vicinity of the interface in the case of ideal contact - condition (7). (*a*) – The entire computational domain in the particle is shown; (*b*) a small region near the boundary is highlighted. It was accepted: $D_p = 5\cdot10^{-6}$; $D_m = 5\cdot10^{-3}$ cm^2/s; $\gamma_0 = 0.999$; time moments: 1– $t = 3\cdot10^{-2}$; 2 – $t = 5\cdot10^{-2}$; 3 – $t = 0.1$ s.
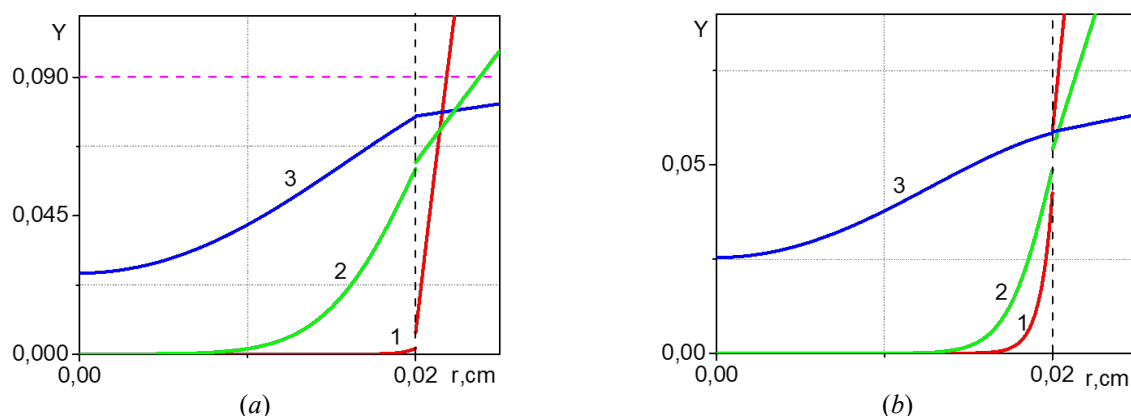

Fig. 5. Diffusant concentration distribution in the vicinity of the interface in the case of non-ideal contact:
(*a*) – condition (6). It was assumed: $D_p = 5\cdot10^{-5}$; $D_m = 5\cdot10^{-2}$; $D_s = 0.16$ cm^2/s; $\gamma = 0.11$;
Time moments: 1 – $t = 1\cdot10^{-2}$; 2 – $t = 2\cdot10^{-1}$; 3 – $t = 1$ s.
(*b*) – condition (8). It was assumed: $D_p = 5\cdot10^{-5}$; $D_m = 5\cdot10^{-2}$; $D_s = 0.16$ cm^2/s;
Time moments: 1 – $t = 1\cdot10^{-2}$; 2 – $t = 5\cdot10^{-1}$; 3 – $t = 1$ s.

4. Conclusion

Thus, the experimental results showed the absence of the expected reactions in the metallothermic mixture. This is presumably due to non-ideal contact between the particles and the melt (due to poor wettability) or between the particles (due to the presence of an oxide film on aluminum). A model of contact formation between the particle and the melt is proposed, taking into account the dependence of the diffusant concentration on the particle surface on the surface tension coefficient and on the surface diffusion coefficient. This stage can be rather long and leads to a delay in the interaction of the main components.

Acknowledgement

5. References

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