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HEAT TRANSFER UNDER PHYSICOCHEMICAL TRANSFORMATIONS

KINETICS OF THERMAL DECOMPOSITION OF ORGANIC BINDERS IN MOLDS

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A set of experiments on determination of the parameters of the gas release from a mold have been performed. The thickness of the casting, the thickness of the mold wall, the process time, and the temperature of the charged metal (liquid gray cast iron) were varied. The investigated molding sands were prepared from quartz sand and organic binders: M19-62 (urea resin), FF-1S (furanic resin), and PK-104 (phenolic resin). On the basis of the experimental data obtained the kinetic parameters of the thermal decomposition of the considered resins have been determined.

Keywords: *mold, synthetic resins, thermal decomposition, kinetics.*

Introduction. The synthetic resins widely used in the foundry to prepare molding and core sands of cold and hot hardening are one of the main sources of pollution of foundries with toxic gases [1]. The estimation of the degree of pollution with gases and the choice of possible measures for lowering it make it possible to improve the working conditions of operational personnel and lower the degree of environmental pollution.

Among the most popular organic binders in molds are synthetic resins of cold hardening that are products of polycondensation of formaldehyde with urea, phenol, and furfuryl alcohol [2]. Of these, urea-formaldehyde (urea) resins feature the lowest thermostability, the highest saturation with nitrogen, and a relatively low binding power, but at the same time they are the cheapest and most readily available. Urea-formaldehyde-furanic (urea-furanic) resins are the easiest to produce and provide a high quality of cores and molds. Therefore, they considerably supersede in the volume of application in the foundry the other classes of acid-hardening resins. Phenol formaldehyde furan (phenol furanic) resins are distinguished by a higher thermostability, which explains their use in producing steel and high-quality pig-iron castings. Phenol formaldehyde (phenolic) resins also feature a high thermostability and are cheaper than phenol furanic resins, but they exhibit a higher toxicity because of the release of phenol vapors.

In the present work, a set of experiments has been conducted with the aim of determining the parameters of the gas release from molds in which the above-mentioned resins are used as binders. On the basis of the experimental data obtained and calculations with the use of the previously constructed mathematical model of molding sand heating [3], we have determined the kinetic parameters of the thermal destruction of these resins.

Experimental. Measurements of parameters of the gas release from a mold charged with a liquid metal were carried out on the experimental facility described in [4]. The facility incorporates an upper heat-insulated half-mold including a cavity to be charged with a liquid metal and a lower half-mold including a heat-insulated cylinder filled with the molding sand being investigated. Below the sand is fixed by means of a net, below which there is a cavity where the molding gases released from the sand are mixed with the carrier gas (e.g., nitrogen or argon). The flow rate of the carrier gas is controlled by a flow transducer precalibrated for a given gas. The current time is counted off from the moment the process of charging the mold with a liquid metal is initiated.

The facility is equipped with an experimental data processing system to which, apart from the carrier gas flow transducer, a humidity detector for molding gases and a block of temperature-sensitive elements distributed throughout the volume of the investigated mold prototype are connected. In a particular case, a flow transducer of undiluted mold

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gases and a molten metal temperature-sensitive element are connected to the system. Signals from all sensors are recorded and computer-processed in a rapid regime.

In the course of the experiments, the investigated molds were charged with liquid gray cast iron. The casting thickness δ and the thickness of the mold wall h were varied over the range of 8–28 mm and 15–100 mm, respectively. The temperature of the charged gray cast iron was varied from 1550 to 1700 K. The molding sands were prepared from 1K02B quartz sand and resins: M19-62 (urea resin), FF-1S (furan resin), and PK-104 (phenolic resin).

The mass release rate of molding gases was calculated from the flow rate of the carrier gas and the concentration of molding gases contained in the sampled gaseous mixture. The chemical composition of the sand was determined by the chromatographic and gas-analysis methods. The main measured process parameter was the volume of released gas $Q = Q(t)$ reduced to normal conditions.

Thermal Decomposition of Resins. Depending on the character of rupture of chemical bonds under thermal destruction, all resins can be divided into two groups [5]. The first group includes resins whose depolymerization is determined by the rupture of the bonds of the main chain with the formation of volatile low-molecular products, i.e., urea resins. The second group includes resins prone to intramolecular detachment of the corresponding functional groups and to cyclization and condensation reactions leading to the formation of a large number of nonvolatile carbonized products (solid carbon). This group contains furanic and phenolic resins.

The elemental composition of the resins used in the experiments and the characteristics of their thermal decomposition are given in Table 1 [6]. The mass fraction of solid carbon C_s and the volume of released gas V were measured for the case of rapid heating of the resin sample to 1700 K (thermal shock). In the absence of experimental data an approximate estimate of these quantities can be obtained on the basis of the elemental composition of the resin on the assumption that its complete decomposition results in the formation of solid carbon and a gas consisting of H_2, CO, and N_2 [6]. In this case, $C_s = 0.01$ (C, mass % − O, mass %), $V = 0.224$ [(1/2) H, mass % + (1/16) O, mass % + (1/28) N, mass %].

Despite the considerable progress in understanding the mechanisms of thermal decomposition of various resins, modeling of the process is restricted, as a rule, to elementary kinetic models describing the starting polymer in general without concrete definition of the products formed (see, e.g., [7]). In the present work, we use the following global kinetic model for describing the thermal decomposition of resins and the passing of destruction products into the gaseous state:

$$\frac{dY}{dt} = -kY\,, \quad k = A\exp\left(-\frac{E}{RT}\right), \qquad Y|_{t=0} = Y_0\,. \tag{1}$$

The solution of Eq. (1) in the one-dimensional statement as applied to the heating conditions of the molding sand in the experimental facility is given by the concentration field $Y(x, t)$ inside the sand:

$$Y(x, t) = Y_0 \exp\left\{-A\int_0^t \exp\left[-\frac{E}{RT(x, t)}\right] dt\right\}. \tag{2}$$

The volume of gaseous destruction products of resin Q that have passed into the gaseous phase in time t is determined by the formula

$$Q(t) = 22.4\rho_{\text{mix}}\varphi_{\text{mix}}h\left[Y_0 - h^{-1}\int_0^h Y(x, t)\,dx\right]. \tag{3}$$

The concentration of the gas-forming fraction in the resin Y at the initial instant of time can be expressed in terms of the V value: $Y_0 = 0.0446V$.

In our previous paper [3], we considered a model problem of the temperature field formation in a baked mold charged with metal with one-sided heat removal through the mold wall on the assumption that the temperature of the liquid metal in the process of its crystallization is constant and the superheating of the metal when charged into the mold is insignificant. Since the concentration of resin in the sand is small, it is assumed that the thermal effect of py-

TABLE 1. Basic Characteristics of the Investigated Resins

Resin	Elemental composition, mass %				Thermodestruction products		T_d, K
	C	H	O	N	C_s	V, nm^3/kg	
M19-62	39.0	6.0	25.0	30.0	0.22	1.26	570
FF-1S	72.0	6.4	21.6	—	0.40	0.94	750
PK-104	78.0	6.1	15.2	0.7	0.50	0.89	760

TABLE 2. Kinetic Parameters of the Process of Thermal Decomposition of Resins

Resin	Y_0, kmole/kg	A, sec^{-1}	E, kJ/mole
M19-62	0.0562	4.0	50.0
FF-1S	0.0421	1.3	66.5
PK-104	0.0399	2.0	66.5

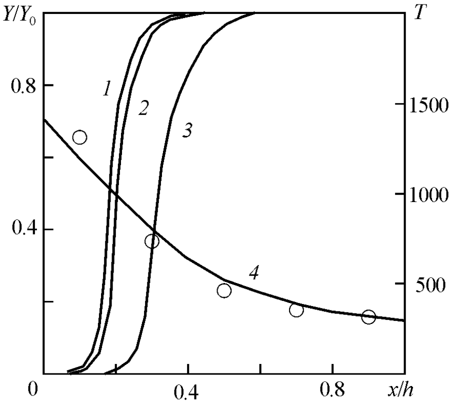
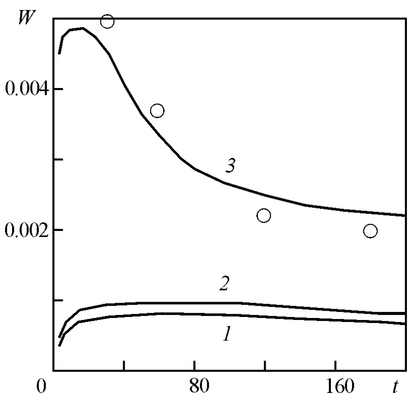


Fig. 1. Calculated distributions of the concentration of the gas-forming fraction of resin (1–3) and the temperature (4) inside the mold: 1) furanic resin; 2) phenolic resin; 3) urea resin. Dots show the measurement data. The process parameters are: h = 100 mm, δ = 28 mm, t = 1900 sec, T_{m0} = 1600 K. T, K.

rolysis reactions, the convective heat transfer by the gas components, and the influence of the change in the sand mass on the temperature field formation can be neglected. The solution of the heat conduction equation in the one-dimensional statement as applied to the heating conditions of the molding sand in the experimental facility permits determining the temperature field $T(x, t)$ with the help of which the concentration field $Y(x, t)$ and the volume of gaseous destruction products of resin Q are calculated by formulas (2) and (3).

Results and Discussion. To calculate the kinetic parameters of the thermal decomposition of resins, we have performed a set of experiments in order to determine the gas release from the mold at the stage of hardening and cooling of the metal casting in a wide range of variation of the process parameters. The thickness of the casting, the thickness of the mold wall, the process time, and the temperature of the charged metal were varied. The kinetic parameters of the process of thermal decomposition were obtained by adjusting the calculated values of the quantity Q to the experimental data with the use of the least square technique. The results of the approximation are presented in Table 2.

Figure 1 shows the calculated and measured temperature fields $T(x, t)$ inside the mold, as well as the concentration curves of $Y(x, t)$ for the investigated types of resins calculated with the use of recovered parameters (see the data of Table 1). Analysis of the figure shows that, all other things being equal, urea resin has the highest thermal decomposition rate. For this resin, the decomposition process begins at a temperature of the order of 600 K, which agrees with the data of Table 1 for the quantity T_d. For furanic and phenolic resins the intensive decomposition temperature is about 800 K. The least resistance of urea resin to temperature loads is also illustrated in Fig. 2 where the dependence of the volume flow of gases W from the mold surface on the process time is shown.



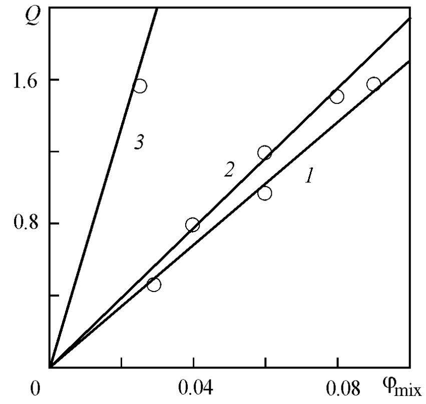
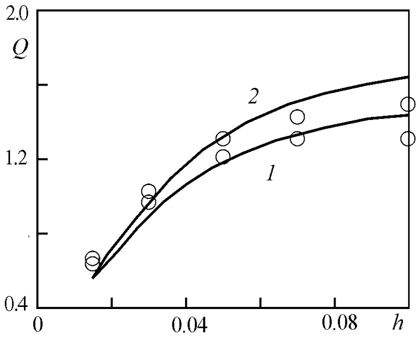


Fig. 2. Volume flow of gases from the mold surface versus the process time: 1) furanic resin; 2) phenolic resin; 3) urea resin. Lines show the calculated data, dots — the experimental data. The process parameters are: h = 50 mm, δ = 28 mm, φ_{mix} = 0.04, T_{m0} = 1600 K. W, nm^3/(m^2·sec); t, sec.

Fig. 3. Volume of released gas versus the content of resin in the molding sand. Lines show the calculated data, dots — the measurement data. Designations 1–3 and the process parameters are same as in Fig. 1. Q, nm^3/m^2.



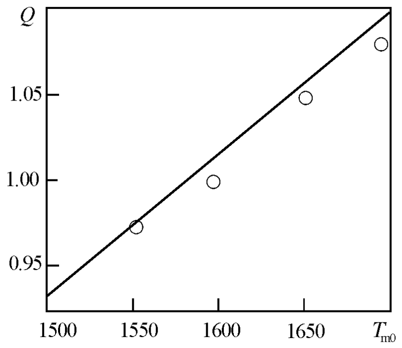


Fig. 4. Volume of released gas versus the thickness of the mold wall for urea resin: a) δ = 18 mm; 2) 28. Lines show the calculated data, dots — the measurement data. The process time is varied from 300 sec at h = 0.015 m to 1800 sec at h = 0.1 m. The process parameters are: φ_{mix} = 0.025, T_{m0} = 1600 K. Q, nm^3/m^2; h, m.

Fig. 5. Volume of released gas versus the temperature of the charged metal for phenolic resin. The line shows the calculated data, dots — the measurement data. The process parameters are: h = 50 mm, δ = 18 m, t = 1080 sec, φ_{mix} = 0.06. Q, nm^3/m^2; T_{m0}, K.

The measurement data for the volume of released gases Q obtained by varying different process parameters (content of resin in the sand, casting thickness, thickness of the mold wall, temperature of charged metal) and their comparison to the calculated data are given in Figs. 3–5. In general, there is a good agreement between the results obtained for all considered variants. It should be noted that the experimental values of Q in Fig. 4 with increasing thickness of the mold wall increase somewhat less rapidly than the calculated ones. This can be due to the influence of the sorption processes that are not taken into account in the calculation.

The measured chemical composition of dry molding gases averaged over the time and the thickness of castings and mold walls is given in Table 3. It is seen that the chemical composition of the molding gases does not depend strongly on the type of resins used in the present work to prepare molding sands. Besides the components given in the table the molding gases contain phenols (0.5% for PK-104 resin and 0.3% for FF-1S resin), formaldehyde (0.2% for

TABLE 3. Averaged Composition of Molding Gases (vol. %)

Resin	H_2	CO	CO_2	CH_4	O_2	N_2	Others
M19-62	46.7	37.7	2.7	2.4	0.4	4.6	5.5
FF-1S	49.0	35.0	1.2	2.8	0.5	4.0	7.5
PK-104	49.6	36.4	0.5	7.7	0.3	2.8	2.9

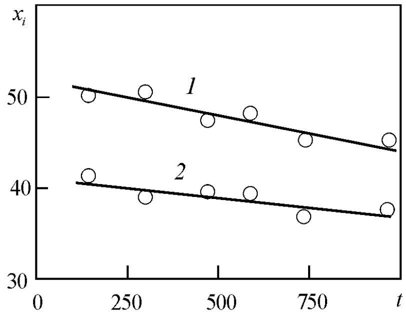


Fig. 6. Change with time in the content of components in the molding gas for urea resin: 1) H_2; 2) CO. Dots show the measurement data. The process parameters are: h = 30 mm, δ = 18 mm, φ_{mix} = 0.025, T_{m0} = 1600 K. x_i, vol. %; t, sec.

M19-62 resin), ammonia (4% for M19-62 resin), hydrocarbons, and other toxic gases. It has also been established that with increasing process time the content of hydrogen and carbon oxide in the molding gas decreases and the content of carbon dioxide increases (Fig. 6).

CONCLUSIONS

1. We have conducted a set of experiments on determining the parameters of the gas release from molds, in which synthetic resins M19-62 (urea resin), FF-1S (furanic resin), and PK-104 (phenolic resin) are used as a binder. The casting and mold thickness, the process time, and the charged metal (liquid gray cast iron) temperature were varied.

2. The kinetic parameters of the thermal decomposition of resins and the passing of destruction products into the gaseous phase have been determined on the basis of adjusting the calculated values of the volume of gaseous products to the experimental data obtained.

3. The main features of the process have been analyzed. It has been shown that, all other things being equal, the highest rate of thermal decomposition is exhibited by urea resin. With increasing thickness of the mold wall the experimental values of the volume of released gas increase somewhat less rapidly than the calculated ones, which can be explained by the influence of the sorption processes. The measured chemical composition of dry molding gases averaged over the time and the thickness of castings and the mold walls does not depend strongly on the type of the resins used.

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NOTATION

A, pre-exponential factor in the rate constant of thermal decomposition of resin, sec^{-1}; C_s, mass faction of solid carbon released from resin due to thermal shock, kg/kg of resin; E, activation energy of thermal decomposition of resin, J/mole; h, thickness of the mold wall, m; k, rate constant of thermal decomposition of resin, sec^{-1}; Q, volume of released gas, nm^3/m^2; R = 8.31 J/(mole·K), universal gas constant; T, temperature, K; T_d, intensive decomposition temperature of resin, K; t, time, sec; V, volume of gas released from resin due to the thermal shock, nm^3/kg of resin; W, volume flow of gases from the mold surface, $nm^3/(m^2 \cdot sec)$; x, linear coordinate inside the mold, m; x_i, molar fraction of the ith gas component; Y, concentration of the gas-forming fraction in resin, kmole/kg of resin; δ, casting thickness, m; φ_{mix}, mass fraction of resin in the molding sand; ρ, plane, kg/m^3. Subscripts: 0, initial value; d, decomposition; m, metal; mix, molding sand; s, solid.

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