INFLUENCE OF GASES ON THE SINTERING OF POROUS SOLIDS

I. INFLUENCE OF GASES ON THE HEALING OF AN ISOLATED PORE

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The kinetics of the change in size of an isolated spherical pore in an isotropic Newtonian medium has been examined in detail by Geguzin [1] for the case where, throughout the whole process, the pore contains no gas, and decreases in size under the action of the surface tension forces $\sigma$ and the external pressure $F_0$ alone. Making the assumption that the rate of deformation is directly proportional to the applied stress, i.e., that $\dot{\varepsilon} = \sigma/\eta$ (where $\eta$ is the viscosity), Geguzin proposes the following formula for the decrease in the radius of the pore as a function of time:

$$\frac{2}{r} \frac{d r}{d t} = - \frac{1}{\eta} \left( \frac{2\sigma}{\eta} + F_0 \right).$$

Ulanovskii and Zhukhovitskii studied the other extreme case [2]. They ignored the action of the surface tension forces and assumed that a pore changes in size solely under the action of the pressure exerted by the gas contained in it. Assuming further that the gas pressure in such a pore is determined by the concentration of gas dissolved in the solid metal and its rate of diffusion toward the pore surface, they derived the following system of equations for the kinetics of the change in pore size:

$$\frac{d c}{d t} = - \frac{22.4NP}{RT} \frac{d V}{d t},$$
$$\frac{d V}{d t} = \frac{RT}{22.4P} K_1 (C - C^6)^{V^{1/3}},$$

where $C$ is the concentration of gas in the metal, $N$ the number of pores, $V$ the pore volume, $P$ the gas pressure in the pore, and $C^6$ the solubility of the gas in the metal at a temperature $T$ and pressure $P$.

As Eqs. (1) and (2) describe only two extreme cases, it is of interest to consider a more general case, where the change in size of a spherical pore in a homogeneous isotropic medium occurs under the action of the Laplacian and external pressures as well as under the action of the gas pressure in the pore.

When a pore is deformed under the action of the pressures mentioned above, we can write

$$\frac{2}{r} \frac{d r}{d t} = - \frac{1}{\eta} \left( \frac{2\sigma}{\eta} + F_0 - P \right).$$

In Eq. (3), the gas pressure in the pore, $P$, is a function of time and pore radius (at constant temperature and given values of physical constants), and is determined by the amount of gas dissolved in the metal and its rate of diffusion toward the pore surface. When the gas pressure in the pore exceeds the equilibrium pressure over a solution of the given concentration, the gas from the pore dissolves in the metal, and its pressure falls. When the gas pressure is less than the equilibrium pressure, gas begins to pass from the metal into the pore, and its pressure in the pore rises.

The flow of gas through the pore surface is described by the equation
Fig. 1. Projections of trajectories on phase plane $(\alpha, y)$ at $F < 1$ (a), $F = 1$ (b), and $F > 1$ (c). The thick, dotted, and thin lines represent separatrices, isoclinics, and trajectories, respectively.

\[ \frac{dQ}{dt} = -\frac{DS}{r} (C - C_0) = -4\pi D r (K \sqrt{P} - C_0), \]  

(4)

where $Q$ is the amount of gas in the pore, $D$ the coefficient of gas diffusion in the metal, $C$ the equilibrium solubility (at a given temperature and pressure $P$) of the gas in the metal, $C_0$ the gas content of the metal, and $K$ the constant in Sievert's equation (for diatomic gases, $C = K \sqrt{P}$).

Taking into account that the gas pressure is related to the gas content of the pore by the expression

\[ P = \frac{3RT}{3Mr} Q, \]  

(5)

where $M$ is the molecular weight, we obtain

\[ \frac{dP}{dt} = -\frac{3RTD}{Mr^2} (K \sqrt{P} - C_0) - \frac{3p}{r} \frac{dr}{dt}. \]  

(6)

Equations (3) and (6) constitute an autonomous system of differential equations determining the kinetics of the change in size of the pore. In its final form, this system is unsolvable.

For a qualitative study of the character of trajectories, it is convenient to change over to the dimensionless coordinates

\[ r = \varepsilon x; \quad p = \rho y; \quad \tau = \frac{2\eta}{p_1} t, \]  

(7)

where

\[ p_1 = \left( \frac{C_0}{K} \right)^2; \quad \varepsilon = \frac{\sqrt{6\eta RTDC_0}}{p_1 \sqrt{M}}. \]  

(8)

The system composed of Eqs. (3) and (6) now becomes

\[ \begin{align*}
\frac{dx}{dt} &= x(y - F) - \alpha \\
\frac{dy}{dt} &= \frac{3ayy}{x} - 3y(y - F) + \frac{1 - \sqrt{y}}{x^2}
\end{align*} \]  

(9)

where the remaining two parameters, $\alpha$ and $F$, are expressed in terms of the starting parameters as follows:

\[ \alpha = \frac{2\sigma}{p_1 \varepsilon} = \frac{2\sigma \sqrt{M}}{\sqrt{6\eta RTDC_0}}; \quad F = \frac{F_0}{p_1} = \frac{F_sK^2}{C_0}. \]  

(10)

For the problems under consideration (where the matrix is a metal and the gas is a mixture of nitrogen, hydrogen, and oxygen), the parameters $\alpha$ and $F$ vary in the ranges $\alpha = 0.01-1$ and $F = 0.1-10^4$. 

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