$\tilde{c}_{z}, \tilde{c}_{p}, \tilde{c}$, Dimensionless concentrations in micropores, macropores, and medium; $c_{p, m}$, mean concentration in a grain, dimensionless; $\tilde{c}_{z}=c_{z} / c_{z o}, \tilde{c}_{p}=c_{p} / c_{0}, \tilde{c}=c / c_{0} ; c_{z}, m$, mean concentration in micropores, dimensionless; $\tilde{r}, R$, dimensionless radial coordinates in micropores and macropores, $\tilde{r}_{z}=r / r_{z}, \tilde{R}=R / R_{p} ; \tau=t D_{z 0} / r_{z}^{2} ; \quad \tilde{D}=D_{z} / D_{z 0} ; v=\frac{3\left(1-\varepsilon_{p}\right)}{\varepsilon_{p}} \frac{c_{z 0}}{c_{p 0}} \frac{1}{\delta} ; \delta=D_{p} r_{z}^{2} /\left(R_{p}^{2} D_{z 0}\right)$; $\lambda=3 \varepsilon_{p} W_{p} /(V \delta) ; \quad B i=B i o t$ number, $S$, parameter in the Langmuir equation; $K$, parameter in the linear-fractional concentration dependence; $W$, $V$, volumes of solid phase and medium; $N$, number of adsorbent particles; $r_{z}$, microcrystal radius; $R_{p}$, grain radius.

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MASS REMOVAL IN FORMATION OF INTERNAL CAVITIES
IN METALS BY CHEMICAL ETCHING
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Mass removal in cavity formation within metals is studied and the principles governing the processes are established.

New methods for chemical etching of metal and alloy surfaces have recently been developed. Ever greater use is being made of forced supply of the liquid reagent to the surface being processed. Thus, for example, it was shown in [1-3] that use of a liquid jet not only allows control of the mass exchange process, but significantly increases the intensity of mass removal in the region of jet interaction with the surface.

The present study will establish the principles of mass removal governing application of a jet of chemically active liquid within a metallic specimen.

Experimental studies have shown that in this situation a cavity which grows in size with time is formed within the metal (Fig. 1). The experiments were performed with full size specimens of the alloy MA-8. Specimen diameter was 110 mm , with a height of 120 mm . Etching was performed by a $7.36 \%$ solution of sulfuric acid in distilled water. An orifice 10 mm in diameter was drilled into the specimen to a depth ho, into which an atomizer with nozzle diameter of 3 mm was installed. To maintain constant flow conditions the distance from the nozzle to the depth ho was kept at 5 mm . The liquid was supplied through nozzle 1 and removed

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Fig. 1. Cavity form: a) $Q=8.7 \cdot 10^{-6} \mathrm{~m}^{3} / \mathrm{sec}, \mathrm{t}=360 \mathrm{~min}$; b) $Q=5.33 \cdot 10^{-6} \mathrm{~m}^{3} / \mathrm{sec}$; solid lines) experiment; points) calculation.
through annular channel 2. The distance $\Delta h_{\text {o could be varied. The specimen was etched for a }}$ given time, then washed, dried, and sectioned in the diametral plane. Cavity depth, solution and specimen temperature, and liquid flow rate were monitored during the experiments. The hydrogen ion content of the solution was determined by titration, and comprised $1500 \mathrm{~g}-\mathrm{eq} / \mathrm{m}^{3}$. The value of the local mass exchange coefficient was determined by measuring the thickness of material $\Delta$ removed over a time $t$. The well known expression of [2], $\beta=\Delta \rho \rho_{M} Z_{M} / A_{M} Z_{H} \cdot c_{0} t$, was used for this purpose. The experiments were performed with flow rates of $1.17 \cdot 10^{-6}-8.83 \cdot 10^{-6} \mathrm{~m}^{3} /$ sec , corresponding to a mean flow velocity $\mathrm{u}_{0}$ at the nozzle section of $0.2-1.3 \mathrm{~m} / \mathrm{sec}$. According to [3], under such conditions the solution of the MA-8 alloy is of a diffusion character.

As is evident from Fig. 1, during its growth the cavity always maintains an elongated form. This indicates that the maximum values of the mass exchange coefficient are realized in the axial region. With some decrease in liquid flow to $Q=5.4 \cdot 10^{-6} \mathrm{~m}^{3} / \mathrm{sec}, \mathrm{Re}_{0}=\mathrm{u}_{0} \mathrm{~d} / \mathrm{v}=$ 3100 the general pattern of cavity growth is maintained, although its growth rate decreases. Further decrease in flow to $\leq 10^{-6} \mathrm{~m}^{3} / \mathrm{sec}$, corresponding to $\mathrm{Re} 0 \leq 500$, leads to formation of a more spherically shaped cavity. This apparently may also be acheived by a significant increase in etching time. In the present experiments the maximum etching time was 8 h . The cavity volume can also be increased by increasing the distance $\Delta \mathrm{h}$ 。 from the nozzle section to the point of flow exit from the atomizer.

To create an adequate model of the cavity growth process the liquid flow during cavity formation was visualized. Experiments were performed involving etching of planar specimens 5-6 mm thick, pressed between Plexiglas plates. It should be noted, however, that the geometry of such a system can be considered planar only a large cavity dimensions. Therefore, the experimental data were used only for qualitative study of the process. Three characteristic flow zones with differing flow hydrodynamics and mass exchange principles can be distinguished in the interaction of the liquid jet exiting the nozzle into the cavity under formation. These are zone I (Fig. 2), the axisymmetric submerged jet which determines the depth of the cavity, zone II, in which formation and development of a fan jet on the wall, flowing upward along a curvolinear surface, and zone III, near the section of liquid exhaust from the cavity. It should also be noted that the process of metal solution and cavity formation proceeds with liberation of gas. Therefore, the upward liquid flow contains two phases. The bubbles are $\leqslant 100 \mu \mathrm{~m}$ in size. According to the data of [3], in a developed turbulent flow the low gas saturation produced by such bubbles does not affect the flow hydrodynamics.

As is evident from Fig. 3, at $t \leq 40$ min the rate of increase in cavity depth is constant, decreasing with further time. This behavior can be explained by the principles of mass exchange in the vicinity of the frontal point of the surface upon impingement of a free jet of incompressible liquid [4] and the propagation laws for a submerged jet [5]. At a constant velocity of jet impingement on an obstacle uo we have [4]

$$
\begin{equation*}
\mathrm{Nu}=0,8 \mathrm{Re}_{0}^{\mathrm{I} / 2} \mathrm{Pr}^{\mathrm{I} / 3} \tag{1}
\end{equation*}
$$



Fig. 2. Diagram of flow in cavity formation.
Here $\mathrm{Nu}=\beta \Delta c / D ; \operatorname{Re}=u_{0} d / \nu ; \operatorname{Pr}=v / D$. During cavity formation the surface moves relative to the nozzle section, due to mass exchange. In this case the characteristics of the incident jet near the etching region will change. According to [5], the boundary of the constant velocity core of an axisymmetric submerged jet $y_{1}$ is given by

$$
\frac{2 y_{1}}{d}=0,224\left(\frac{x+x_{0}}{d}\right)+0,0015 \sqrt{2}\left(\frac{x+x_{0}}{d}\right)^{2}
$$

while the maximum velocity profile along the submerged jet axis

$$
\begin{gather*}
u_{m}=u_{0} \quad \text { at } x / d \leqslant 4,12 \\
u_{m}=\frac{5,12}{x / d+1} \text { at } x / d>4,12 \tag{2}
\end{gather*}
$$

If we assume that at a given distance $x$ the velocity of the jet incident on the boundary can be calculated with Eq. (2), i.e., decreases with increase in cavity depth, then the law of mass exchange in the axial zone of the cavity will be determined in the following manner:

$$
\begin{gather*}
\text { at } x / d \leqslant 4,12-\text { formula }(1) \\
\text { at } x / d>4,12 \quad \mathrm{Nu}=0,8 \operatorname{Re}_{0} \operatorname{Pr}^{1 / 3}\left(\frac{5,12}{x / d+1}\right)^{1 / 2} \tag{3}
\end{gather*}
$$

A calculation of the rate of increase in cavity depth with these expressions is shown in Fig. 3. The agreement of the mass exchange coefficients with the calculated values indicates the validity of the assumptions made. The slight difference is apparently related to the presence of a counterflow which brakes the liquid jet exiting from the nozzle. In this case the calculation can easily be corrected by replacing the coefficient 5.12 in Eq. (3) by 4.12 . However, it should be noted that a large times ( $t \geq 8 \mathrm{~h}$ ) the calculation will obviously diverge greatly from experiment due to noncorrespondence of the model considered with the real flow pattern. In fact, as $t \rightarrow \infty$ we have a flow pattern with an axisymmetric point source.

To describe the process of cavity growth in the zone of formation and development of the fan jet on the wall it is first necessary to know the hydrodynamics of development of such a jet with a source on the axis of rotation. The principles of propagation and interaction with a wall of a plane submerged turbulent jet have been established previously [6]. In [7] this theory was extended to a plane fan jet. We will present results for the interaction of a submerged fan jet with a wall of arbitrary curvature. The pattern of flow development is shown in Fig. 4.

Neglecting centrifugal effects and the curvature of the surface ( $\delta d^{2} r / d R^{2}(1+(d r)$ $\left.\left.\mathrm{d} R)^{2}\right)^{3} / \mathbf{2}\right) \ll 1$, we write the equations of the boundary layer for developed turbulent flow on on a body of rotation [8]

$$
\begin{equation*}
u \frac{\partial u}{\partial r}+\tau \frac{\partial u}{\partial y}=\frac{1}{\rho} \frac{\partial \tau}{\partial y} \tag{4}
\end{equation*}
$$



Fig. 3


Fig. 4

Fig. 3. Increase in depth of axisymmetric cavity $\left(Q=5.33 \cdot 10^{-6} \mathrm{~m}^{3} /\right.$ sec ): I) calculation by Eq. (1); II) by Eq. (3). $x, m ; t$, min.

Fig. 4. Pattern of fan jet.

$$
\begin{equation*}
\frac{\partial}{\partial r}(u R)+\frac{\partial}{\partial y}(v R)=0 \tag{5}
\end{equation*}
$$

From this it is simple to obtain $\frac{d}{d r} \int_{0}^{8} \rho u^{2} R d y=-\tau_{w} R \quad$ (where $\tau_{w}$ is the friction on the cavity surface). If we consider that at $y=\delta_{m}$ the velocity $u$ takes on its maximum value $u_{m}$ ( $y=\delta_{m}, d u / d y=0, u=u_{m}$ ), then we have

$$
\begin{equation*}
u_{m} \frac{d}{d r} \int_{0}^{\delta_{m}} \rho u R d y-\frac{d}{d r} \int_{0}^{\delta_{m}} \rho u^{2} R d y=\tau_{w} R \tag{6}
\end{equation*}
$$

Using the concepts of displacement depth $\delta *$ and momentum loss thickness $\delta * *$, we arrive at the expressions

$$
\begin{equation*}
R u_{m} \delta^{* *}\left[\frac{\delta^{*}}{\delta^{* *}}-\frac{\delta_{m}}{\delta^{* *}}+1\right] \frac{d u_{m}}{d r}+u_{m} R \frac{d}{d r}\left(u_{m} \delta^{* *}\right)+u_{m}^{2} \delta^{* *} \frac{d R}{d r}=\tau_{w} R \tag{7}
\end{equation*}
$$

We use the following dimensionless variables and parameters:

$$
\begin{aligned}
R / d & =\bar{R} ; \quad r / d=\bar{r} ; \quad \bar{u}_{m}=u_{m} / u_{0} \\
\operatorname{Re}^{* *} & =u_{m} \delta^{* *} / v ; \quad c_{f} / 2=\tau_{w} / \rho u_{m}^{2}
\end{aligned}
$$

where $d$ is the diameter of the channel from which the axisymmetric jet exits with initial velocity $u_{0}$. Then the momentum integral relationship Eq. (7) takes on the form

$$
\begin{equation*}
\frac{d \mathrm{Re}^{* *}}{\overline{d r}}+\left(\frac{\delta^{*}}{\delta^{* *}}-\frac{\delta_{m}}{\delta^{* *}}+1\right) \operatorname{Re}^{* *} \frac{d \ln \bar{u}_{m}}{d \bar{r}}+\mathrm{Re}^{* *} \frac{d \ln \bar{R}}{d \bar{r}}=\frac{c_{f}}{2} \mathrm{Re}_{0} \bar{u}_{m} \tag{8}
\end{equation*}
$$

Using a power law $u / u_{m}=\left(y / \delta_{m}\right)^{1 / n}$ for the velocity distribution in the wall boundary layer, we have

$$
\begin{gathered}
\frac{\delta^{*}}{\delta_{m}}=\frac{1}{n+1} ; \frac{\delta^{* *}}{\delta_{m}}=\frac{n}{(n+1)(n+2)} \\
1+\delta^{*} / \delta^{* *}-\delta_{m} / \delta^{* *}=-(n+1)
\end{gathered}
$$

As usual, the friction law is determined by the Blasius expression [8]:

$$
\begin{equation*}
c_{f} / 2=B\left(\mathrm{Re}^{* *}\right)^{-m} \tag{9}
\end{equation*}
$$

where $\mathrm{n}=7, \mathrm{~m}=0.25, \mathrm{~B}=0.0128$.

To solve Eq. (8) we must know the dependence of $\bar{u}_{m}$ on $\bar{r}$. We will assume that in a submerged turbulent jet on a wall the law of conservation of quantity of motion within the flow [7] is satisfied approximately

$$
\begin{equation*}
\int_{0}^{\delta} 2 \pi \xi u^{2} d y=\frac{\pi d^{2} u_{0}^{2}}{4} \tag{10}
\end{equation*}
$$

where $\xi=R(r)-y \cos \alpha(r)$.
In submerged jets the velocity profile is adequately described by the law [8]

$$
\begin{equation*}
u / u_{m}=\left[1-(y / \delta)^{3 / 2}\right]^{2} \tag{11}
\end{equation*}
$$

Substituting Eq. (11) in Eq. (10), we obtain

$$
\begin{equation*}
\int_{0}^{1}(R / \delta-\eta \cos \alpha)\left(1-\eta^{3 / 2}\right)^{4} d \eta=\frac{d^{2} u_{0}^{2}}{8 u_{m}^{2} \delta^{2}} \tag{12}
\end{equation*}
$$

It has been established experimentally [5] that $\delta(r)$ depends linearly on $r: \delta(r)=0.22 r$. After calculations we have

$$
\begin{equation*}
\bar{u}_{m}^{2}=\frac{1,8}{\bar{r}(\bar{R}-\bar{r} \cdot 0,046 \cos \alpha)} \approx\left(\frac{1,34}{\sqrt{\bar{r} \bar{R}}}\right)^{2}=\frac{c_{1}^{2}}{\bar{r} \bar{R}} \tag{13}
\end{equation*}
$$

With consideration of Eqs. (9), (13), Eq. (7) transforms to the equation

$$
\begin{equation*}
\frac{d \mathrm{Re}^{* *}}{d \bar{R}}+\frac{(n+1)}{2} \mathrm{Re}^{* *}\left(\frac{1}{\bar{R}}+\frac{d \ln \bar{r}}{\overline{d R}}\right)+\frac{\mathrm{Re}^{* *}}{\bar{R}}=B \mathrm{Re}_{0} c_{1} \mathrm{Re}^{* *-m} \frac{1}{\sqrt{\bar{R} r}} \frac{\overline{d r}}{d \bar{R}} \tag{14}
\end{equation*}
$$

with initial condition $\operatorname{Re} * *(b)=$ Reo**, where $b$ is a point on the initial section of the fan jet [6]. For convenience we have transformed to the variable $\bar{R}$ here. With the substitution $f=\operatorname{Re} * *(I+m)$ this nonlinear Bernoulli equation transforms to a linear equation [9], upon solution of which we obtain

$$
\begin{equation*}
\operatorname{Re}^{* *}=\left(\frac{b}{\bar{R}}\right)^{\frac{n+3}{2}}\left(\frac{\bar{r}(b)}{\bar{r}}\right)^{\frac{n+1}{2}}\left[\operatorname{Re}_{0}^{* *(m+1)}+B(m+1) \operatorname{Re}_{0} c_{1} \int_{0}^{\bar{R}} \frac{\overline{d r^{\prime}}}{\sqrt{\bar{r}^{\prime} \bar{R}^{\prime}}}\left(\frac{\overline{R^{\prime}}}{b}\right)^{\frac{(n+3)(m+1)}{2}}\left(\frac{\overline{r^{\prime}}}{\bar{r}(b)}\right)^{\frac{(n+1)(m+1)}{2}}\right]^{\frac{1}{1+m}} \tag{15}
\end{equation*}
$$

We are concerned with the self-similar asymptote of the fan jet in its main portion, therefore, as in [6], we will consider the limit $b \rightarrow 0, \bar{r}(b) \rightarrow 0$ :

$$
\begin{equation*}
\operatorname{Re}^{* *(1+n)} \rightarrow B(m+1) \operatorname{Re}_{0} c_{1} \times \int_{0}^{\bar{R}} \frac{d \bar{R}^{\prime}}{\sqrt{\bar{r}^{\prime} \bar{R}^{\prime}}} \frac{d \bar{r}^{\prime}}{d \bar{R}^{\prime}}\left(\frac{\bar{R}^{\prime}}{\bar{R}}\right)^{\frac{(n+3)(m+1)}{2}}\left(\frac{\overline{r^{\prime}}}{\bar{r}}\right)^{\frac{(n+1)(m+1)}{2}} \tag{16}
\end{equation*}
$$

From Eqs. (9) and (16) we have

$$
\begin{equation*}
\frac{c_{f}}{2}=B \mathrm{Re}^{* *-m}=0,276 \mathrm{Re}_{0}^{-0,2} \times\left[\int_{0}^{\bar{R}} \frac{d \bar{R}^{\prime}}{\sqrt{\overline{r^{\prime}} \bar{R}^{\prime}}}\left(\frac{\overline{d r^{\prime}}}{d \bar{R}^{\prime}}\right)\left(\frac{\overline{R^{\prime}}}{\bar{R}}\right)^{6,75}\left(\frac{\overline{r^{\prime}}}{\bar{r}}\right)^{5}\right]^{-0,2} \tag{17}
\end{equation*}
$$

For calculations it will be convenient to transform from the local friction coefficient $c_{f}$ to the coefficient $c_{f o}$, defined from the velocity head in the nozzle:

$$
\begin{equation*}
\frac{c_{f 0}}{2}=\frac{\tau_{w}}{\rho u_{0}^{2}}=\frac{c_{f}}{2} u_{m}^{2}=\frac{c_{f}}{2} \frac{c_{1}^{2}}{\bar{r} \tilde{\mathrm{R}}}=0,9 \frac{c_{f}}{\bar{r} \vec{R}} \tag{18}
\end{equation*}
$$

Local mass removal from the cavity boundary is determined by the flow hydrodynamics. This process is characterized by large diffusion Prandtl numbers ( $\operatorname{Pr}=v / D \gg 1$ ). The diffusion layer "sinks" in the viscous sublayer of the dynamic boundary layer. Then transport of the material due to turbulent perturbations penetrating into the viscous layer from the turbulent region of the flow becomes comparable to molecular diffusion. Modeling the turbulent viscosity coefficient in the viscous sublayer by a fourth power law [10], we obtain

$$
\begin{equation*}
\mathrm{Nu}=0,119 \mathrm{Pr}^{\mathrm{I} / 4} \mathrm{Re}_{0} \sqrt{c_{f 0} / 2} \tag{19}
\end{equation*}
$$

where the numerical value of the coefficient in Eq. (19) is taken from experimental data [11]. The value of the friction coefficient $c_{f}$ o has been found above, Eq. (18). The number $N u$, as was noted above, determines the local rate of cavity growth, directed perpendicular to the cavity surface:

$$
\begin{equation*}
v_{n}=\frac{\beta \Delta c}{\rho_{\mathrm{M}}}=\mathrm{Nu} \frac{\Delta c D}{d \rho_{\mathrm{M}}} \tag{20}
\end{equation*}
$$

Equations (19), (20) can be used to numerically calculate the dynamics of cavity growth for an arbitrary initial geometry. It proves to be the case that use of the six-point Simpson formula for numerical integration of Eq. (17) provides sufficient speed and accuracy for engineering purposes. The results of a numerical calculation with these expressions are presented in Fig. 1. It is evident that for the etching times studied the calculation describes the cavity form satisfactorily, with the exception of the zone where the flow exits the cavity.

The results obtained may be used for calculation and analysis of processes related to preparation of internal cavities in metal parts without altering their external shape.

## NOTATION

$t$, Time, sec; $\Delta$, thickness, $m$; $\beta$, mass exchange coefficient, $m / s e c ; ~ \rho_{m}, m e t a l$ density, $\mathrm{kg} / \mathrm{m}^{3} ; \mathrm{zM}, \mathrm{zH}$, valence of metal and hydrogen; $\mathrm{AM}_{\mathrm{M}}$, atomic weight of metal; c , concentration, $\mathrm{g}-\mathrm{eq} / \mathrm{m}^{3}$; $u$, velocity, $\mathrm{m} / \mathrm{sec} ; \mathrm{d}$, nozzle diameter, $\mathrm{m} ; ~ v$, kinematic viscosity of liquid, $\mathrm{m}^{2} / \mathrm{sec}$; $D$, diffusion coefficient, $\mathrm{m}^{2} / \mathrm{sec} ; \mathrm{x}, \mathrm{y}$, coordinates, $\mathrm{m} ; \delta *$, displacement depth, $\mathrm{m} ; ~ \delta * *$, momentum loss thickness, $m$; $c_{f}$, resistance coefficient; $\mu$, dynamic viscosity, $\mathrm{kg} / \mathrm{m}^{2} \cdot \mathrm{sec} ; \mathrm{Re}$, Reynolds number; Pr, Prandtl number; Nu, Nusselt number.

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