E-16 Effect of Capillary Action on Fracture Due to Liquid Metal Embrittlement

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ABSTRACT

An analysis is presented of the influence of capillary action on fracture due to the liquid metal embrittlement of solid metals. This work discusses the conjecture that capillary action enhances the penetration of liquid metals into solids. Contrary to statements by other investigators, it is suggested in this paper that high pressures may not arise in the process of liquid metal embrittlement. A Poiseuille type of flow model is postulated and a prediction made therefrom of crack length growth with time. Some verification is obtained with experimental observations.

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INTRODUCTION

The embrittling effect produced by liquid metals on stressed solid metals is a well-known phenomenon.(1) [3] However, the mechanism which precipitates this effect is still not clearly understood. This paper gives further serious attention to the influence of capillary action on this phenomenon.

A recent paper by N. S. Stoloff and T. L. Johnston (2) proposed an interesting mechanism for crack propagation in a liquid metal environment. If the stress necessary to extend a crack is based on the rupture of atomic bonds by tensile stress at the tip of the crack, there is a decrease in fracture stress and the amount of plastic deformation accompanying the crack propagation. It is postulated that the liquid in contact with the tip of the crack lowers the binding energy of the unbroken atomic bonds defining the tip of the crack. Also, it was speculated that a similar process accounts for crack nucleation. Although grain boundaries offer preferred nucleation sites, they need not play a predominant rôle in liquid metal embrittlement. A. R. C. Westwood and M. H. Kamdar (3) proposed a mechanism similar to Stoloff and Johnston's in which local cohesion is reduced by a strain activated chemisorption process. They suggest that the elastic strain in the vicinity of the crack tip causes chemisorption of the liquid metal either by supplying activation energy or by producing atomic geometric configurations which allow electronic interaction.

Elbaum (4) found in experiments on pure, fully annealed, unstressed aluminum wetted with liquid gallium that penetration along grain boundaries occurred at a very slow rate. He concluded from his study that the phenomenon is more likely controlled by diffusion in the liquid rather than by diffusion in the grain boundary. He indicated that the gallium would dissolve an amount of aluminum which would be deposited on the surface of the grain boundary. It was felt that this process would be controlled by the rate at which aluminum could diffuse in liquid gallium and consequently, would terminate when the grain boundary would be replaced by a layer of liquid. Presumably, if his specimens had been stressed, the penetration rate would have been much more rapid. Nichols and Rostoker (5) suggested that the liquid metal reduces by an adsorption process the surface energy for generating and propagating the crack. Other investigators have given some consideration to the mechanisms of liquid metal embrittlement involving chemical reactions. Rhines, et.al.(6) carried out a series of bend tests on aluminum and brass wetted by mercury and examined, among other things, the effect of temperature and pressure on crack propagation growth.

Smith (7) theorized that capillary action is the mechanism by which the liquid metal penetrates the solid metal. Also, he states that the liquid proceeds along the grain boundaries, prying apart the grains and completely disintegrating the solid. Another viewpoint on the disintegration of the solid is that the actual deterioration of material

[3] Superscripts in parentheses denote references which are collected at the end of the paper.

properties is a manifestation in some way of the Rebinder effect. Likhtman, Rebinder, and Karpenko (8) consider the potential effect of capillary action in their investigation of surface-active media. They indicate that high capillary pressure could arise but conclude that this is improbable because viscous effects prohibit capillary entry of the liquid medium into the solid. Moreover, they contend that penetration of the liquid "is obviously not based on the induction of a liquid of given viscosity into a system of capillaries according to the laws of hydrodynamics."

An analysis is given below to demonstrate that fluid velocities, derived under the assumption that capillary action is a significant driving mechanism, are indeed of the order of the magnitude of those determined from experiments.

ANALYSIS

As a mathematical model of the physical problem, it will be assumed that the liquid metal flows in a channel of constant radius r; the surface tension forces T are inclined at the contact angle θ with the flow direction, as shown in Fig. 1. If the fluid stress p behind the meniscus is assumed equal to the axial force divided by the channel area, the stress becomes

$$p = \frac{(T\cos\theta)\ 2\ \ r}{r^2} = \frac{2T}{r}(\cos\theta) \qquad (1a)$$

In order to determine the crack velocity V, a Poiseuille model of flow behavior is used, namely, viscous, laminar channel flow. The pressure drop p in a channel of length L is given by the expression

$$p = \frac{8\,L\,\mu\,V}{r^2} \qquad (1b)$$

where μ is the coefficient of viscosity and V is the average fluid velocity. If the driving force is assumed to arise from capillary action, this is equivalent to assuming the flow being drawn rather than pushed.[4]

If Eq. (1a) is substituted into Eq. (1b), the velocity becomes

$$V = \frac{T\,r\,(\cos\theta)}{4L\,\mu} \qquad (2)$$

[4] There is good cause to expect the tensile field in the fluid to be sustained without the formation of voids. Capillary action on both sides of the opening (as well as an induced vacuum) would tend to close any openings should they arise in the fluid line.

The following estimates will be used for order of magnitude purposes:

$$\left.\begin{aligned} \cos\theta &= 1 \\ L &= 1 \text{ cm} \\ \mu &= 0.016 \text{ poise} = 0.016 \text{ dyne-sec/cm}^2 \\ 2r &= 10^{-3} \text{ cm} \\ T &= 400 \text{ dyne/cm} \end{aligned}\right\} \quad (3)$$

For this order of magnitude analysis, it is assumed that the liquid metal properties are those of mercury, and that perfect wetting occurs, i.e., $\theta = 0$. The values of μ and T were obtained from Ref. 9 and the value of 2r from p. 53 of Ref. 1. Consequently, the velocity calculated from Eq. (2) is of the order of those determined experimentally (1)

$$V = 1.2 \frac{in}{sec} = 3.1 \frac{cm}{sec}$$

In order to examine how the liquid fills the channel with respect to time, Eq. (2) is rewritten in the following form:

$$V = \frac{dL}{dt} = \frac{Tr\ (\cos\theta)}{4L\mu}$$

If T, r, μ, and θ are assumed to be constants, then the above equation, upon integration, becomes

$$L^2 = \frac{(T\ r\ \cos\theta)}{2\mu}\ t + C$$

From the initial condition

$$L(0) = 0,$$

it follows that

$$C = 0$$

and the above expression may be put in the form

$$L^2 = Kt \quad (4a)$$

$$K = \frac{T\ r\ (\mathrm{Cos}\ \theta)}{2\mu} \quad (4b)$$

Experimental results showing the variation of crack length with time were found in Ref. 1; these results are reproduced in Fig. 2. It was noted in Ref. 1 (p. 53) that most experimental evidence indicates that the crack and fluid velocities are approximately equal. Therefore, it

appears reasonable to compare the present theoretical results of Eq. (4a) with the aforementioned experimental data (Ref. 1, p. 43).

In order to examine whether or not Eq. (4a) offers a reasonable approximation to the actual situation, the constant K is calculated from a point on Fig. 2. For t = 14 sec. it is seen that L = 5.58 in. Then

$$K = 2.21 \text{ in}^2\text{/sec} \quad (5)$$

With this value for the constant, corresponding L and t values are obtained and plotted as crosses on the experimental curve of Fig. 2. As can be readily seen, the agreement is excellent.

To show that the previous order-of-magnitude argument is still consistent with the present results, the values given in Eqs. (3) and (5) are substituted into Eq. (4b). The value of K so obtained is of approximately the same order of magnitude as Eq. (5).

It is significant to note that the capillary driving forces can be estimated, using the values of Eq. (3) in Eq. (1a), to be of the order of 12 psi. Should the liquid metal source be at an elevated pressure, say 15 psi gage, the crack velocities will approximately double. These results are in general agreement with experimental results (see Ref. 1, p. 52).

In addition, it might be mentioned that gravity pressures for crack lengths of the order of one inch are about 1/2 psi. While this is not too significant relative to capillary driving pressures, it should certainly be sufficient to cause the liquid flow to choose the easiest path, namely in the direction of the gravity force. Again, this is in accordance with experimental observations (Ref. 1, p. 51).

The addition of gallium to mercury greatly increases the embrittling effect on aluminum (Ref. 1, p. 77). This may be attributed at least in part to the fact that surface tension of gallium is more than 50% greater (10) than mercury, possibly permitting easier capillary penetration.

CAPILLARITY AND PRESSURE AS DRIVING FORCES

Rhines, et.al. (6) implicitly suggested that atmospheric pressure is the primary driving force on the liquid metal for tests performed at room conditions.

Experiments were carried out on brass subjected to bending loads and exposed to liquid mercury at a pressure of two atmospheres. A significantly greater crack propagation rate was observed for this case than at one atmosphere. Subsequently, experiments were performed with mercury at a reduced pressure. The lower pressure was obtained by creating a vacuum over the mercury source and applying cellulose tape in the region of expected crack growth. In this experiment, a significantly reduced crack propagation rate was observed. However, one possible reason for this result is that the atmospheric pressure may have been transmitted to the liquid mercury source through the cellulose tape creating a "back pressure" which could seriously inhibit the mercury flow. From the calculations in the preceding section, the value of the stress due to the capillary effect is of the order of the atmospheric pressure. Should this be the case, it is indeed possible for the capillary pressure to be equilibrated by the induced back pressure resulting in an extremely small amount of flow. In order to assess this point more accurately, an experiment should be carried out when the entire specimen is in a vacuum.

Rhines, et.al.[6] assumed a Poisseuille type of flow model as used in Eq. (1b) of this paper. If the pressure at the liquid metal source is the only significant driving mechanism, then it is evident from Eq. (1b) that a liquid with lower viscosity should permeate through the solid metal much more effectively. However, water and a variety of other liquids which have significantly less viscosity than liquid metals cause virtually no embrittling effect. On the other hand, there is a significant difference between the surface tension of liquid metals, water, and other liquids.

It is interesting to note that the crack propagation rate determined by Rhines, et.al.[6] is equal to the value calculated in this paper if the wetting angle equals 60°. The crack propagation rate, however, determined in this paper is directly related to the surface tension which is not considered in Ref. 6.

As pointed out in Ref. 1, should the external pressure be the only driving force, a pressure of the order of 10^5 atmospheres would be necessary to cause the mercury to reach the crack tip. On the other hand, it should be readily possible to have the material transported to the crack tip via a capillary effect. (This point is discussed further in the next section).

Indeed, the actual driving mechanism for transporting the liquid metal may be some combination of pressure and capillarity. To include the effect of pressure, it would only be necessary to add one other term in Eq. (1a). As a result, an additional pressure term would evolve in the constant K in Eq. (4b); however, Eq. (4a) would remain unchanged except for the value of K.

DISCUSSION

In the present paper, quantitative arguments are given to support the conjecture that capillary action may contribute to a driving mechanism causing penetration of a solid by a liquid metal. Some corroboration with experimental results is obtained.

Likhtman, Rebinder, and Karpenko[8] stated that a hydromechanic analysis could not predict the penetration characteristics of a liquid metal; they also took the position that high capillary pressures could arise if viscous effects were small. In the present paper an analysis is performed wich is based on a hydromechanics approach to the penetration characteristics of a liquid metal. Also, from the model adopted in the present paper, a tensile rather than a compressive field persists in the fluid; hence high pressures cannot arise independent of whether viscous effects are significant. Kramer came to a similar conclusion for different reasons [11].

While the analysis presented here concludes that capillary pressure does not seriously influence crack propagation, it further suggests that capillary action may be a mechanism by which the liquid metal is transported to the vicinity of the crack root. However, no attempt has been made to discern the cause of crack initiation. In this connection, it should be mentioned that results presented here are not contradictory with previously mentioned theories for crack initiation.[2,3] These theories require the presence of the liquid metal at the crack tip. It should not be difficult to imagine the channel of Fig. 1 to narrow at a conically shaped end section. In accordance with Eq. (2) the velocity should decrease linearly with the radius; but from the conservation of mass the velocity should increase as the square of the radius. The net effect would be for the fluid velocity to increase or accelerate to the crack tip. This would occur continuously or intermittently as the fluid flows.

The effect of a tensile field in the solid metal is twofold: (a) greater voids due to deformation permit easier capillary entry and (b) fracture under a tensile field could more easily be effected if the filled liquid metal capillaries are considered as a multitude of internal imperfections which cause many stress concentrations. Should the field be compressive, both the above phenomena would be less likely to occur which suggests that no embrittling effect should occur. This is in agreement with experimental observations.

The present analysis may be extended to obtain the properties of the fluid or those of the propagating crack in the material. Also the above relations may be used with suitable elasticity and plasticity solutions, or failure criteria, such as given by A. A. Griffith and G. R. Irwin, to determine stresses in a material, or limiting values of residual and applied stress. In addition, it appears possible to determine some of the properties of the physical parameters of the fluid provided that the values are given for the applied stress and material constants. The authors of this paper are presently engaged in such studies.

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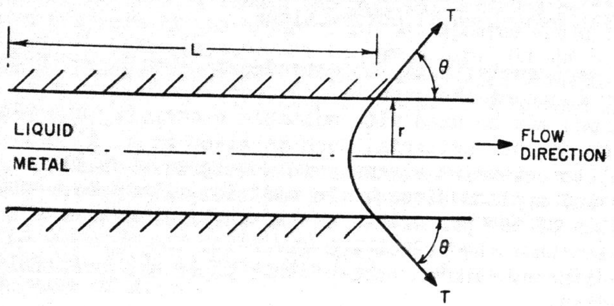

FIG. 1 MODEL OF FLOW BEHAVIOR

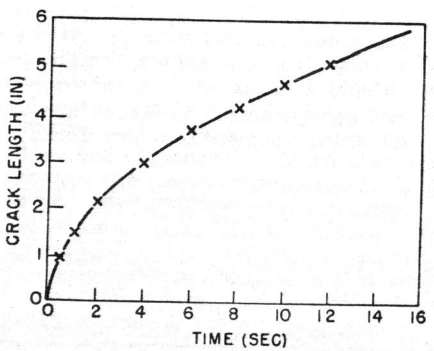

FIG. 2 CRACK LENGTH VS. TIME