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DIFFUSION-CONTROLLED DECOHESION USING A Cu-Sn ALLOY AS A MODEL SYSTEM

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ABSTRACT

This research deals with a mode of brittle intergranular fracture in which a surface-adsorbed embrittling element is driven into a grain boundary as a result of the application of a tensile stress across the boundary. A Cu-8%Sn alloy has been employed to explore this phenomenon, since tin is a surface-active element, and this alloy is known to suffer intergranular weakness at elevated temperatures. Intergranular cracking occurred by brittle, discontinuous crack advance at 265°C in vacuum with an average rate of 0.1µm/sec. This behavior is analogous to sulfur-induced stress-relief cracking in steels and several cases of liquid-metal embrittlement, suggesting that this phenomenon has a generic nature.

INTRODUCTION

The presence of embrittling elements at interfaces, such as the grain boundaries in a polycrystalline material, can lead to brittle, intergranular fracture. The source of the embrittling element can be either external to the material, i.e., its gaseous, liquid, or solid environment, or the material itself in the form of solute impurities or alloy elements. Solute atoms can contaminate the grain boundaries by *segregation* as a result of a heat treatment prior to mechanical testing, causing intergranular cracking at low temperatures or high strain rates. The low mobility of solute atoms at a low temperature precludes atomic diffusion to the tip of a growing crack, and fracture occurs at a high speed. Notable examples are the temper embrittlement in steels [1] and segregation-induced embrittlement of Ni by S [2]. However, contamination of the grain boundaries from an external or internal source can occur in metallic alloys as a result of application of a stress during mechanical testing. When a material which is normally ductile, is loaded at a temperature where *grain boundary penetration by diffusion* of an embrittling element contained on a free-surface can occur, it can crack slowly along the grain boundaries. Examples include the brittle mode of stress relief cracking (SRC) in steels [3], and solid- and liquid-metal embrittlement of steels by Cd and In [4], and of aluminum alloys by Hg [5] and Ga [6,7].

In this report we are concerned with the problem of intergranular cracking at elevated temperatures which is induced by an embrittling element which penetrates the grain boundaries from a surface as a result of the drop in chemical potential caused by the application of a tensile stress across the boundary. A Cu-8wt% Sn alloy has been chosen to explore this phenomenon, since tin bronzes with tin content higher than 5% are known to show a pronounced tendency to intergranular cracking in hot working, and tin is a surface-active element in this alloy [8]. Our preliminary results have shown [9] that a quasi-static intergranular cracking occurs in this alloy in the temperature range 265 to 300°C in UHV under dead-loading conditions. Tin was found to contaminate the free surfaces of this alloy by surface segregation at the test conditions, and it was proposed [9] that surface-segregated tin enriches the grain boundaries of the material at the crack tip area by stress-assisted diffusion, resulting in slow cracking, apparently due to loss of cohesion along the grain boundaries. This cracking appears to be analogous to the brittle mode of SRC in steels.

Kanno et al [10, 11] have also shown that intergranular cracking in this alloy is enhanced at low strain rates at about 300°C, but they attributed this type of fracture to intergranular segregation of sulfur. Our surface-segregation experiments [9] showed no evidence that sulfur is a mobile impurity in our alloy, and tensile tests at room temperature showed no intergranular embrittlement.

The cracking behavior of this Cu-Sn alloy was investigated by means of slow-strain-rate tensile tests in vacuum in the temperature range 230 to 300°C. The results are analyzed to test the

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proposed model for cracking involving stress-induced penetration of grain boundaries by a surface-adsorbed embrittling element.

EXPERIMENTAL PROCEDURE

A laboratory heat of a Cu-8%Sn alloy, commercially called "phosphor bronze", was prepared by vacuum-induction melting and casting in argon. The tin content of the alloy was verified using gravimetric analysis. Circumferentially-notched tensile specimens, the dimensions of which are shown in Fig. 1, were machined from both as-cast and homogenized material. The specimens were vacuum-annealed at 600°C for one hour to stabilize the microstructure.

Prior to the tensile tests in vacuum (10^{-5} - 10^{-6} Torr), the specimens were heated in the test chamber at 400°C for 1 hour in 1 atm hydrogen to remove contamination of the notch root by oxygen and carbon [9]. The system was allowed to stabilize at the test temperature for about one hour, and the chamber was evacuated before loading. Some of the specimens were loaded at a relatively high cross-head speed (CHS) just below the point where load drops were observed in a preliminary test at 256°C. Then, the CHS was reduced to a slower one at which no load drops were observed. The load on the specimen and the cross-head displacement were recorded as a function of time.

The fracture surfaces of specimens that failed at high temperature were examined using scanning electron microscopy. In addition, longitudinal metallographic sections of specimens from tests interrupted at various crack-growth stages were examined using optical microscopy.

RESULTS AND DISCUSSION

In a typical tensile test at 265°C, the notched-bar specimen was loaded at a relatively high CHS (0.01 in/min) up to a maximum load in the range of 500 to 550 lbs, before the CHS was reduced to a slower one, as Fig. 2(a) shows. After some further specimen extension at the slow CHS, load drops were detected. Since there was no change in the specimen dimensions during the test, except in the notched portion of the failed specimen, the displacement of the cross-head associated with the load drops was considered to be the result of cracking in the notched portion. The part of a load vs. time curve of Fig. 2(a), which exhibited these discontinuous load drops, is presented in Fig. 2(b). At the onset of slow crack growth, load drops of the order of 10 lbs were observed, with a waiting time of several minutes between drops. The waiting times decreased as the test proceeded.

Fractographic examination of the surface of the specimen that failed at 265°C in vacuum revealed that fracture took place with minimal overall plasticity. (The ring of fine-grained material at the root of the notch is due to recrystallization of material which had been deformed during the machining of the notch.) The fracture appearance was macroscopically brittle and almost completely intergranular, as shown in Fig. 3(a).

Some regions of ductile tearing and shear were observed between regions of intergranular cracking; it is believed that these regions correspond to rupture of remaining ligaments which held the intergranularly separated areas together. Closer examination at higher magnification revealed that the grain faces were decorated with "ripples", which appear similar to fatigue striations (Fig. 3(b)). The spacing between the striations varies from 2 to 10 μm ; more closely-spaced lines (1-2 μm) were also observed between the major ones in some areas. The major striations are probably due to crack opening after the crack arrests following load drops. Some of these major striations were found to continue across grain boundaries.

Fig. 1 Design of the cylindrical, notched specimen used in tensile tests.

Fig. 2 (a) Load vs. time curve of a tensile specimen of the Cu-8wt% Sn alloy tested at 265°C in vacuum. (b) Expanded load vs. time curve for a portion of the test exhibiting discontinuous cracking at a slow strain rate.

The intergranular cracking appears to have occurred by brittle, discontinuous crack advance as a result of decohesion on a micro-scale. The presence of the minor striations indicates that the fundamental microcracking mechanism operates on smaller distance and time scales than the macroscopic crack jumps. Thus, it appears that between each macroscopic crack jump a microfracture process occurs. We believe that this microcracking mechanism involves the stress-induced diffusion of surface-segregated tin from the surface of the newly created microcracks to the boundary ahead of the crack tip. Decoherence is thought to result when a critical combination of tin concentration and tensile stress is reached. This process repeats itself and leads to step-wise crack growth on a micro scale. When several of these microcrack fronts coalesce, a macroscopic crack jump may take place, producing a load drop. In the notched-bar tests, crack jumps of the order of micrometers several minutes apart resulted in an average crack velocity of 10^{-6} to 10^{-7} m/sec, in good agreement with the crack-growth rates measured in compact-tension specimens using the potential-drop method [9].

The fact that the fracture process is stress-controlled is demonstrated by the occurrence of the cracking in the regions of high stress: the notch roots and the center of the reduced section, as Fig. 4 shows. In addition, the temperature dependence of this process is illustrated by the load vs. time curves of Fig. 5. The plot of the times required to reach a load level of 300 lbs vs. the inverse temperature (Fig. 6) indicates an Arrhenius type of relationship with an activation energy of about 20 Kcal/mole. This activation energy compares well with the activation energy of the grain boundary diffusivity of tin in our copper alloy, which has been estimated from the bulk diffusivity ($Q_1 = 42$ Kcal/mole) measured by Hoffman and Erlewein [8].

Fig. 4 Longitudinal metallographic section of a tensile specimen loaded at 300°C in vacuum at a slow strain rate to the onset of load drops.

Fig. 3 (a) Fracture surface of the tensile specimen of Fig. 2, showing brittle intergranular cracking. (b) Part of the intergranular facet indicated by the arrow in (a), suggesting that crack growth occurred in steps normal to the direction of the striations.

(a)

(b)

Fig. 5 Load vs. time curves for tensile specimens tested at different temperatures in vacuum.

An expression for the crack-growth rate has been derived using the diffusion equation with a $\sigma\Omega$ potential term and with a fracture criterion which employs a relationship between the stress to fracture vs. the impurity concentration. The details of this model are described elsewhere [12], but an average crack-growth rate can be calculated from the following expression:

$$\dot{a} = \alpha \frac{D_{gb}\Omega}{kT} \frac{C_0}{C^*\sigma^*} \frac{\sigma_y^2}{\delta_t}$$

where $\alpha = 3$ to 9 m/s is a numerical constant, D_{gb} the grain boundary diffusivity of tin in copper, Ω is the activation volume of tin, T is the temperature of the test, C_0 the equilibrium surface concentration of tin in this alloy at the test temperature, $C^*\sigma^*$ is estimated from the experimental data by Kameda [13], σ_y is the yield stress of the material at the test temperature, and δ_t the crack-tip radius. At the conditions of the test, and with a reasonable choice of the above parameters ($\alpha = 6$ m/s, $D_{gb} = 4.2 \times 10^{-14}$ m²/s, $\delta_t = 100$ nm) the crack-growth rate was calculated to be 1.2×10^{-7} m/s, which approximates the experimentally measured cracking rates.

It must be recognized that this diffusion-controlled-decohesion mechanism can be operative in any case where an embrittling element present at the crack tip can be driven by the applied stress into the solid. It has already been associated with the brittle mode of stress-relief cracking in steels, where sulfur plays the same role as the tin in this copper alloy [9]. Similarly, some cases of liquid-metal embrittlement, like the embrittlement of a B-brass single crystal by Ga [14,15], exhibit the same macroscopic cracking behavior, i.e., discontinuities in the load vs. displacement curve accompanied by striations on the fracture surface, indicating some kind of time-dependent cracking. The cracking kinetics may be controlled either by the transport of the embrittler to the crack tip or the stress-induced penetration by diffusion, but this question remains to be answered by further study.

Fig. 6 Temperature dependence of the time required to reach 300 lbs for tensile specimens tested at a slow strain rate in vacuum.

CONCLUSIONS

- 1) A quasi-brittle intergranular fracture has been achieved in a phosphor bronze alloy tested in the temperature range 230 to 300°C.
- 2) This fracture appears to be the result of intergranular decohesion caused by surface-adsorbed tin which is thought to be driven from the surface to the boundaries by the applied stress.
- 3) A model based on the idea of diffusion-controlled decohesion leads to an estimate of the crack-growth rate corresponding to the experimentally measured rate.
- 4) Solid- and liquid-metal embrittlement may be related phenomena that can be treated by this model.

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