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QUASI-STATIC INTERGRANULAR CRACKING IN A Cu-Sn ALLOY; AN ANALOG OF STRESS RELIEF CRACKING OF STEELS

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E. V. Barrera*, M. Menyhard**, D. Bika, B. Rothman***, and C. J. McMahon, Jr.

ABSTRACT

Intergranular cracking in a laboratory-made Cu-8wt%Sn alloy at 265 to 300°C in vacuum was studied in order to explore the hypothesis that this could serve as an analog to the brittle mode of stress-relief cracking in steels and to test the mechanism proposed earlier to explain that phenomenon. This mechanism involves the stress-induced intergranular penetration along grain boundaries of a surface-adsorbed embrittling element. Sulfur is the active element in this regard in steels, and tin was envisioned as playing the same role in Cu-Sn alloys. Auger spectroscopy was used to confirm earlier reports of the surface activity of tin and to determine the segregation kinetics in the present polycrystals; no other elements were found to segregate to surfaces to any significant degree in the present alloy. Crack growth measurements showed that intergranular cracking occurs in an intermittent manner at an average rate on the order of 0.1μm/sec over a range of crack length. Crack initiation was found to be remarkably sensitive to the stress intensity, implying the existence of a threshold. The fracture appearance in the regions of slow crack growth was similar to that observed in steels undergoing stress-relief cracking at 500-600°C. It was concluded that the quasi-static intergranular cracking in the steels and in the Cu-Sn alloy represent two aspects of the same generic phenomenon and that the proposed mechanism of stress-induced intergranular impurity penetration is valid. It is believed that liquid- and solid-metal embrittlement are closely related to the type of intergranular cracking described here.

INTRODUCTION

This report is related to the general problem of time-dependent intergranular fracture which appears to result from a loss of cohesion along grain boundaries, induced by the concentration of an embrittling element in the boundaries *as a result of* the application of a stress. That is, the grain boundaries are initially uncontaminated, and the material is ductile except when it is loaded in the presence of an element concentrated on the surface in a temperature range where grain-boundary diffusion of that element can occur. In the broadest sense, this encompasses liquid- and solid-metal embrittlement, as well as cracking

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induced by an external source of hydrogen, but here we are concerned with the case in which the source of the surface contaminant is the material itself. That is, the contaminant exists in solid solution as an impurity or as an alloy element.

The prototypical example of this phenomenon is the brittle mode of stress-relief cracking (SRC) in steels, which has been shown conclusively [1,2] to be the result of the contamination of grain boundaries by sulfur during loading at temperatures in the 500 to 700°C range. The sulfur is made available by a prior high-temperature treatment which partially dissolves sulfides, followed by cooling at a rate sufficiently rapid to restrict re-precipitation of the sulfur. (Some re-precipitation may occur at the austenitic grain boundaries to which the released sulfur has segregated.) The most striking feature of this brittle mode of SRC is that, although the cracking occurs at rates in the range of 0.1 to 1 μm/sec, the resulting fracture can be essentially indistinguishable in appearance at high magnification from intergranular brittle fracture at low temperatures, which occurs at rates orders-of-magnitude greater.

Several conflicting mechanisms have been proposed to account for this phenomenon. One [1] is an extension of the mechanism of diffusive growth of creep cavities, in which atoms from the surface of the cavity are "plated out" in the grain boundary around the cavity in exchange for vacancies which enlarge the volume of the cavity. The driving force is the work done by the tensile stress acting across the boundary as the specimen extends in this direction owing to the addition of the atoms to the boundary. The extension of this model to the cracking phenomenon rests on the proposition that, if the surface of the cavity is contaminated by an impurity which can cause decohesion, then, in the presence of a sufficiently high stress, the cavity could grow in a crack-like manner by loss of cohesion in the surrounding grain boundary.

Thus, we have proposed [1] that the brittle mode of SRC proceeds by the segregation of sulfur to the free surface of a crack and the subsequent diffusion of the sulfur into the grain boundary ahead of the crack, thereby allowing decohesion in the sulfur-enriched region. An alternative proposal [2,3] has been made to the effect that the sulfur segregates to internal grain boundaries directly from solid solution, in response to the elastic stress field near a crack tip, in the manner of solute segregation to an edge dislocation [4]. The experimental evidence for step-wise crack growth provided by observations of fracture-surface striations [3,5] and acoustic emissions [6] does not distinguish between these two proposals.

It can be reasoned that, if the former hypothesis is correct, then it should be possible to produce analogous cracking in other systems which contain a potential surface-active embrittling element. To explore this further, experiments have been carried out on an alloy of Cu-8wt%Sn. These were motivated by three facts: First, it has been reported by Kanno et al. [7,8] that brittle intergranular fracture occurs in tensile tests of this alloy at elevated temperatures. Secondly, tin is a well-known embrittling element in steels, and one could postulate that it could play a similar role in copper alloys, since this has been found to be the case for antimony [9], which behaves similarly to tin in alloy steels [10,11]. Thirdly, tin is known to be surface-active in Cu-Sn alloys, and the kinetics of tin segregation to the free surface of monocrystals have been measured [12].

The approach in the present work was to load clean compact-tension specimens of the Cu-Sn alloy at temperatures around 275°C, which would be analogous to 600°C in a steel (where stress-relief cracking can occur), under conditions in which tin is known to segregate to the surface. Hence, the surface at the tip of a crack or cavity could be assumed to be contaminated by tin, and the system would be analogous to that postulated for SRC in steels. Preliminary observations have been made, and the anticipated cracking has been observed; the results are reported here.

EXPERIMENTAL PROCEDURE

An alloy of Cu-8wt% Sn was made in the laboratory by vacuum melting OFHC copper and high-purity tin and casting in an argon atmosphere. The composition of the alloy is given in Table I. The alloy was hot rolled to a thickness of about 15 mm, and it exhibited a pronounced tendency for cracking, especially at the edges of the plate. This is consistent with the known [13] tendency of commercial bronzes of this composition to be "hot short", i.e., to crack during hot working. It was possible to trim away cracked portions and to retain a sufficient amount of uncracked material to make test specimens. The grain size after hot rolling was 20 μm, and the material was tested in this condition.

The crack-growth was studied on side-grooved compact-tension specimens the dimensions of which are shown in Fig. 1, and the constant-load tests were carried out in the apparatus depicted in Fig. 2. Tests were carried out in the temperature range 250 to 325°C in a vacuum in the range 1 to 4 x10^{-8} Torr. Prior to the test, the specimen was cleaned in the test chamber by heating to 400°C in one atmosphere of hydrogen; the efficacy of this cleaning will be described below. The crack growth was monitored by means of a microcomputer-controlled reversing DC potential-drop method. The configuration of current and voltage leads was the one optimized in a finite-element study by Aronson and Ritchie [14]. During the tests the ratio of the electrical resistance of the cracking specimen with respect to a reference resistance was recorded as a function of time. The crack length corresponding to each resistance ratio was obtained from an experimental calibration curve of resistance ratio *vs* crack length.

RESULTS

Specimen Cleaning. Our intention was to explore the effect of surface-segregated tin on the otherwise-clean surface of the Cu-Sn alloy. Cleaning of the CT specimen in the testing chamber by the traditional method of ion sputtering was impracticable, so a hydrogen treatment at an elevated temperature was used. In order to establish the conditions needed for surface cleaning, experiments were carried out in a separate UHV system with the configuration shown in Fig. 3. A small polished sample of the alloy was heated at various temperatures and hydrogen pressures in a side chamber which could be valved-off from the main chamber used for Auger electron spectroscopy. It was found that the optimum cleaning was achieved at 400°C in one atmosphere of hydrogen. An example of the effect of this treatment is shown by the Auger spectra in Fig. 4. Whereas the surface before the treatment contained adsorbed carbon and oxygen, a one-hour treatment in hydrogen at 400°C removed all the carbon and most of the oxygen. In the few cases that sulfur contamination was observed, this was also removed by the hydrogen treatment. This treatment of 400°C in hydrogen was carried out on all CT specimens before the temperature was reduced to the desired test temperature, the test chamber evacuated, and the load applied.

Crack-Growth Measurements. The cracking behavior of the Cu-Sn alloy can be illustrated by the results of a test carried out at 265°C. The crack length is plotted as a function of time in Fig. 5(a), and the applied loads during each time period are shown in Fig. 5(b). High loads were applied initially in order to begin the crack growth from the initial slot, which was produced by electric-discharge machining. It can be seen that a load of 640lb got the cracking process started. The load was then reduced to 220lb and then increased in steps in order to find a load where slow cracking could be observed in a reasonable time; this was finally achieved at a load of 460lb. The portion of the curve of crack length *vs* time at this load was smoothed using Fourier-transform filtering of 20-point-wide blocks of data points and the smoothed curve is shown in Fig. 6(a). This curve was then differentiated using centered differences to give the plot of crack velocity *vs* time shown in Fig. 6(b). The accuracy of the measurements of crack length is estimated to be ±0.05mm.

The intermittent crack growth depicted in Fig. 6 was found in all specimens tested, and it was also found in alloy steels specimens treated so as to be sensitized to SRC and tested in the same way at 550°C [15]. It can be seen that the maxima at times less than 400sec. in the plot in Fig. 6(b) occur at a cracking rate of approximately 0.1 μm/sec.

Fracture Appearance. After the crack-growth observations, the specimens were fractured at room temperature. This fracture took place by plastic rupture and large-scale plastic deformation of the specimens, indicating that the grain boundaries of the material were not embrittled in the traditional sense. However, the cracking at the [illegible] temperature had proceeded with only minimal overall plasticity. The mode [illegible]he early stages of crack growth at 265°C, as shown in Fig. 7, was almost completely intergranular. As the cracking proceeded, the incidence of plastic tearing and shear between regions of intergranular cracking increased until the final stage, which was almost entirely plastic, as shown by the fractographic montage in Fig. 8. Thus, the intergranular mode was characteristic of relatively slow crack growth; as the increase in stress intensity drove the crack faster, the mode shifted gradually to the normally one found at low temperatures.

Observations of Free-Surface Segregation. In order to assess the probable surface condition during crack growth, polished specimens were mounted in a PHI 600 scanning Auger spectrometer and heated at various temperatures after various amounts of cleaning by sputtering. It was found that, after repeated heating and ion sputtering, only tin would segregate to the surface. An example of this at 400°C is shown in Fig 9(a). However, after less-extensive sputter cleaning, carbon would also be found to segregate, as shown, for example in Fig. 9(b). This carbon is believed to have come from solid solution in the alloy, not from the vacuum chamber. Therefore, it must be concluded that the surfaces of the crack-test specimens contained some segregated carbon as well as tin. There is no reason to believe that this carbon played a role in the cracking process. It should be noted that no sulfur was observed to segregate.

The segregation of tin occurred rapidly and reached a saturation level of 18 to 25at%, as given by the system software of the spectrometer, which is based on the methods given in reference 16. This level may be compared with the 30at% reported by Hofmann and Erlewein [12] for a Cu- 0.5at%Sn (111) surface. Since the calibration procedures are different for the two sets of observations, and the present ones were made on polycrystals, they cannot be said to show a significant disagreement.

The rapidity of the tin segregation, in contrast with the much slower segregation observed in single crystals [12], is interpreted as the result of short-circuit diffusion along grain boundaries to the free surface in the present polycrystals with a 20μm-dia. grain size. An indication of that could be obtained by scanning the primary beam of the scanning Auger microprobe across a grain boundary during heating of the specimen, as shown in Fig. 10; the concentration on the surface increased first in the vicinity of the grain boundary. The saturation level of around 20 to 25% could be the result of depletion of the near-surface grain-boundary regions, rather than a manifestation of thermodynamic equilibrium. In any case, that is the relevant concentration for the present crack-growth experiments.

DISCUSSION

As seen in Fig. 8, the initial part of the crack growth at 265°C is almost entirely intergranular. It resembles closely the appearance of the brittle mode of stress-relief cracking in steels [1,2]. At the resolution of the SEM, the intergranular facets are smooth, and they exhibit large areas with no sign of cavitation. Thus, they appear to be the result of decohesion.

It must be emphasized that this alloy does not show any tendency toward intergranular brittleness when tested at a rapid strain rate either at low temperatures or at temperatures up to, at least, 300°C. Therefore, whatever the level of tin segregation to the grain boundaries prior to a test, it is insufficient to produce traditional intergranular embrittlement in an alloy as ductile as this Cu-8wt%Sn. (The level of equilibrium segregation of tin to grain boundaries cannot be determined by the usual method of fracture in UHV and analysis by AES precisely because the grain boundaries are not embrittled.) Therefore, we are forced to the conclusion that the observed intergranular decohesion at about 0.4 of the liquidus temperature and at a rate of about 0.1μm/sec is due to some dynamic effect which occurs during the application of stress.

Figure 5 shows that the rate of crack growth is remarkably sensitive to the applied load, that is, to the stress intensity, and that some threshold stress intensity is necessary to get the process started. This can be seen from the effect of reducing the load from 460 to 400lb after the crack had begun to accelerate; a subsequent increase to 440lb was not sufficient to re-establish the rapid growth, which only started again when the former level of 460lb was re-applied.

The ductility minimum at 500 to 600°C observed by Kanno and Shimodaira [8] in tensile tests at a strain rate of around 10^{-3}/sec was attributed by them to intergranular segregation of sulfur, a residual impurity. The problem with this explanation is that it does not address the fact that the ductility passes through a minimum at high temperatures but is not impaired at lower temperatures. If the intergranular strength is reduced by segregation of some element *before*, rather than *during*, the test, then the ductility should be low at all temperatures. Also, in the present study, the surface-segregation experiments showed very little evidence that sulfur was a mobile impurity in this alloy, and tensile tests at room temperature and below showed no evidence of any intergranular embrittlement.

Kanno et al. [7] showed that the tendency for intergranular fracture became greater as the strain rate was decreased in their tensile tests. This effect was large in their tests at 300°C. Therefore, the present observations of intergranular brittleness in statically loaded specimens at that temperature are completely consistent with their results. There is no reason to believe that the two sets of observations relate to other than the same phenomenon. For the reasons given earlier, the intergranular weakening must stem from a dynamic phenomenon which takes place only during the application of stress. We postulate that this phenomenon is exactly analogous to that proposed earlier for SRC of alloy steels (stress-induced penetration of grain boundaries by a surface-adsorbed embrittling element).

The surface analysis of specimens treated in the same way as the CT fracture specimens has shown that no relevant embrittling element other than tin is present on the cleaned and heated surface of this alloy. Therefore, the only surface element which could have penetrated the grain boundaries under stress is tin. Therefore, we have demonstrated that the phenomenon of sulfur-induced stress-relief cracking of alloy steels [1] can be replicated in the Cu-Sn alloy. This supports the hypothesis that these observations represent two aspects of the same general phenomenon of diffusion-controlled decohesion.

It may be noted that steels with free sulfur share another characteristic with the Cu-Sn alloys: They are both hot short. That is, they both exhibit intergranular brittle cracking during hot deformation, like forging or rolling. We suggest that this is another manifestation of the same general phenomenon. The rate of impurity penetration increases with stress; therefore, whatever retards stress-relief by plastic flow must enhance this kind of cracking. For this reason the hydrostatic tension which can occur in a body during deformation processing is an ideal state of stress to promote this type of cracking.

It must be recognized that the present results have not *disproved* the two existing alternative hypotheses [2, 3, 17] offered to explain sulfur-induced SRC in steels; however, they certainly do not support them. Chen [17] has treated the problem as a diffusive growth of a crack-like cavity, not involving decohesion, based on the postulated effects of sulfur on the dihedral angle at the cavity tip and on the diffusion coefficient in grain boundaries. This model can be criticized in terms of its inadequacy to explain the recently observed rates of cracking in steels; this inadequacy would be much worse in a Cu-Sn alloy, given the lower surface activity and mobility of tin in copper, compared with sulfur in steel.

Hippsley et al. [2,3] have proposed that the decohesion in SRC actually occurs in the traditional way at grain boundaries in the high-stress region ahead of a crack tip, and that this is a result of enhanced segregation of sulfur (an undersize atom) to iron grain boundaries under the influence of the hydrostatic tension in this region. Notwithstanding the absence of a physical basis for this hypothesis, it would seem unlikely to apply to both the case of sulfur in iron and that of (oversize) tin in copper.

SUMMARY

Slow crack growth at 275 to 325°C in vacuum was studied in an alloy of Cu-8%Sn to test the hypothesis that it could serve as a model material for the phenomenon of diffusion-controlled intergranular brittle fracture, the best-known example of which is stress-relief cracking in alloy steels at 500 to 600°C. The segregation of the embrittling element tin to the crack surface in a CT specimen was intended to be analogous to the segregation of sulfur to a crack surface in a steel. It was found that the Cu-Sn alloy does, indeed, behave in a way essentially identical to the steel containing free sulfur. Quasi-static intergranular fracture, resembling decohesion, occurs at a rate of about 0.1μm/sec under conditions in which tin is the only element present on the crack surface. The cracking occurs intermittently, rather than smoothly, and there is a sharp threshold in stress intensity for the onset of observable crack growth, which implies the existence of the classical form of log crack velocity *vs* stress intensity curve. The results are consistent with the proposed mechanism for stress-relief cracking which entails stress-driven diffusion of a surface-adsorbed impurity along grain boundaries and subsequent decohesion when a critical level of the impurity concentration is reached.

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FIGURE CAPTIONS

1. Design of CT specimen.
2. System for testing under constant load in UHV at elevated temperatures.
3..Layout of chambers used for hydrogen treatment of specimens and Auger electron spectroscopy.
4. Auger spectra from polished sample of Cu-Sn alloy (a) before and (b) after a one-hour treatment in hydrogen in a UHV chamber at 400°C.
5. (a) Crack length *vs* time at 265°C from potential-drop measurements at applied loads indicated in (b).
6. (a) Smoothed data for crack length *vs* time for a load of 460lb at 265°C. (b) Crack velocity *vs* time found by differentiating the curve in (a).
7. Intergranular cracking mode in an early stage of slow crack growth at 265°C.
8. An extended view of the fracture surface at 265°C, showing the transition from smooth intergranular fracture in the initial stages to increasing amounts of plastic tearing as the crack length (and velocity) increases.
9. (a) Increase of tin concentration with time at 395°C on the surface of a sample extensively cleaned by ion-sputtering (b) Increase in carbon concentration with time on the surface of a less-extensively sputtered sample heated at 420°C and the concomitant decrease in tin concentration.
10. Results of AES scans across a grain boundary intersecting the surface of a polished and sputtered specimen heated at 150°C for increasing amounts of time, showing that tin arrives at the surface more rapidly along the grain boundary than from the bulk.

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