

TIME-DEPENDENT INTERGRANULAR BRITTLE FRACTURE

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ABSTRACT

Two forms of time-dependent brittle cracking along grain boundaries are compared here. Both of these involve diffusion-controlled decohesion, but in one case, the diffusing species is hydrogen and in the other it is a surface-adsorbed embrittling element. The application of a tensile stress in each case serves both to concentrate the diffusing species at the tip of a sharp crack and to provide the force necessary to overcome the bonding along the grain boundaries. In both cases the cracking rate depends on the structure of individual grain boundaries, but in the case of hydrogen it appears to be necessary that the grain boundaries be previously contaminated with some level of an embrittling impurity. In the other case, the grain boundaries may be completely uncontaminated prior to the application of stress; here, the embrittling process is inherently dynamic, not only because it is time-dependent but also because it depends on the application of a force (*dynamis* in Greek).

1. INTRODUCTION

There are two well-recognized types of time-dependent intergranular brittle fracture. One is hydrogen-induced cracking of high-strength steels, and the other is the phenomenon that has come to be called dynamic embrittlement. It is instructive to compare the two, because there are important points of similarity that can aid in understanding of the mechanisms involved. Both of these phenomena occur by the growth of sharp cracks controlled by the diffusion of an embrittling species. Both occur at rates that depend on the structure of individual grain boundaries. Both occur as a result of the application of a tensile stress, and the susceptibility to both increases with the strength of the material. It is important to realize that the growth of a sharp crack implies that the decohesion process takes place on the near-atomic scale.

2. HYDROGEN-INDUCED INTERGRANULAR BRITTLE CRACKING

It is generally recognized that hydrogen-induced cracking of high-strength steels occurs along prior austenite grain boundaries. However it is not as widely recognized that this is not an effect of hydrogen alone, but rather the effect of hydrogen plus some amount of prior impurity segregation at these boundaries. This can be shown most clearly from results on a 5% Ni that was aged at 480°C to allow segregation of P to produce temper embrittlement [1], as shown in Fig. 1. Before the aging treatment, the failure in hydrogen occurred at a high stress intensity, and the mode of cracking was transgranular (with respect to the prior austenite phase). This cracking occurred along planes of maximum shear stress, and it was related to plastic flow, presumably because of hydrogen carried along in the cores of dislocations [2]. This means that hydrogen alone does not cause intergranular fracture, probably because it does not segregate to grain boundaries to an extent sufficient to cause decohesion, even at a very high stress. However, it is apparent that with even a small amount of aging the threshold stress intensity for cracking in hydrogen is reduced precipitously, and this is associated with the appearance of intergranular decohesion.

In a study of the interaction of hydrogen with specific embrittling elements in a Ni-Cr steel, Kameda used laboratory heats doped with Sb, Sn, or P, for which he had previously determined the value of the critical local tensile stress σ^* for intergranular fracture in air in notched bars loaded in pure bending [3]. This was done as a function of the maximum value of the intergranular impurity concentration (determined from AES measurements and a statistical analysis) in specimens that had been aged at 480°C. When these experiments were repeated in hydrogen, he found that the critical stress for intergranular microcrack initiation σ_{th} was lower than σ^* , as shown in Fig. 2 [4]. The stress at which fracture occurred in hydrogen σ_H^* was intermediate

between σ^* and σ_{th} . The interpretation was that σ_H^* represents the stress for rapid crack propagation in either air or hydrogen, assuming that hydrogen does not affect rapid fracture. This means that σ^* is the stress for microcrack *initiation* in the absence of hydrogen, and that the stress for crack propagation has already been exceeded. In the case of the Sb-doped steel the value of σ_{th} reached a plateau at high Sb concentrations because it could not fall below the stress for plastic yielding, which is required to nucleate the microcrack [3].

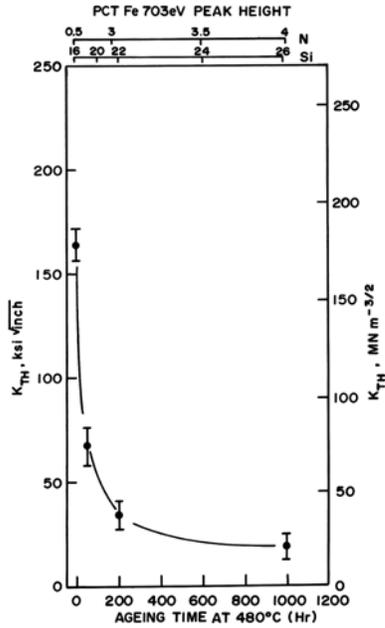


Fig. 1 Effect of aging at 480°C on the threshold stress intensity for hydrogen-induced cracking in a production heat of HY 130 steel with a yield strength of about 910MPa [1].

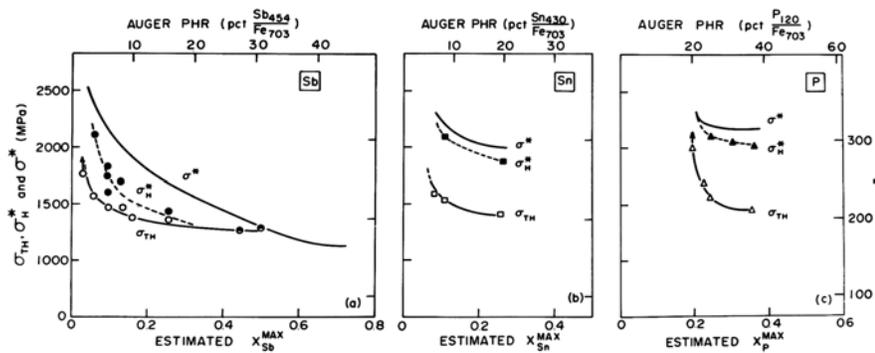


Fig. 2 The effect of increasing the maximum concentration of Sb, Sn, or P in the grain boundaries of a Ni-Cr steel on the stress σ^* to produce brittle intergranular fracture in air, the stress σ_{th} to produce an intergranular microcrack in hydrogen, and the stress σ_H^* to cause brittle intergranular fracture in hydrogen. After Kameda [4].

The values of σ^* shown in Fig. 2 were determined by loading specimens in hydrogen for an extended time and then breaking them open by fatigue in air to look for the presence of an intergranular microcrack [4]. This first microcrack was always found some distance ahead of the notch tip, indicating that the hydrogen had diffused inward to the most embrittled grain boundary that lay within the region of maximum tensile stress ahead of the notch. This is to be expected in view of the well-known effect of hydrogen of expanding the crystal lattice of iron.

As in other cases of brittle fracture in steels, microcrack initiation starts when slip is blocked by an inclusion. In this case it involves a non-metallic inclusion lying in a prior austenite grain

boundary [4]. The presence of hydrogen in the high-stress region ahead of the notch allows a microcrack to form at a stress lower than would be required in the absence of hydrogen. Kameda and Jokl [5] have offered an explanation of how this could happen: In the absence of hydrogen, when a microcrack nucleus is formed at an inclusion, it can either grow into an observable microcrack or not, depending on the stress level. In the presence of hydrogen, the microcrack nucleus can gather up hydrogen as it extends, because of the lattice expansion at the tip of this sharp crack, as shown schematically in Fig. 3. The increasing hydrogen concentration in the crack-tip region provides an additional reduction in the cohesive strength of the grain boundary that already contains some level of an embrittling element. This allows the microcrack to grow to a size large enough to detect, but the microcrack arrests when it reaches a grain boundary that is less embrittled or when it extends beyond the high-stress region. This embrittlement by hydrogen is an inherently dynamic process in which the cohesive strength of a grain boundary is progressively reduced as an extending crack tip sweeps up hydrogen in its core. This requires that an intergranular microcrack first be initiated, which is the role of the segregated impurity. Thus, the intergranular cracking in hydrogen can occur when the impurity level in the grain boundaries is not high enough to produce intergranular fracture on its own.

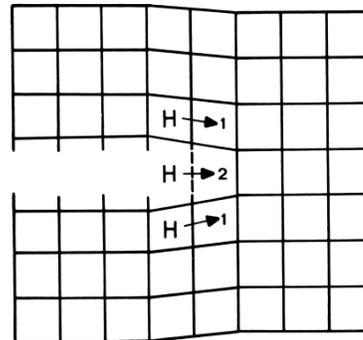


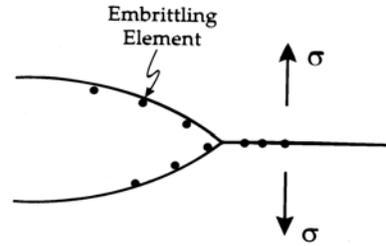
Fig. 3 Schematic representation of the expanded lattice at the tip of a sharp crack, which can gather up hydrogen as the crack extends. After Kameda and Jokl [5].

3. DYNAMIC EMBRITTLEMENT

Dynamic embrittlement is physically related to the phenomenon of intergranular hydrogen-induced cracking. Both involve the propagation of a sharp crack because of an applied tensile stress that drives a fast-diffusing embrittling element into the crack-tip region. That is, the applied stress is responsible for the gradient in chemical potential that drives the diffusion. Of course, it also supplies the force necessary to overcome interatomic bonding along the grain boundaries. There are two important differences between the two phenomena: First, the diffusing atom in dynamic embrittlement, while more mobile than the atoms that comprise the alloy, is much less mobile than hydrogen. Secondly, the grain boundaries do not need to be contaminated *a priori* with an embrittling element in the case of dynamic embrittlement, whereas they do in the case of hydrogen-induced cracking. The embrittling elements responsible for dynamic embrittlement are potent enough to lead to decohesion on their own, but this is not the case for hydrogen acting alone. Another incidental difference is that the variation in cracking susceptibility among grain boundaries, while it depends on grain-boundary structure in both cases, comes from the effect of structure on impurity segregation in the case of hydrogen, but on impurity diffusivity in the case of dynamic embrittlement.

The mechanism of dynamic embrittlement is best envisioned in terms of the classical Hull-Rimmer [6] mechanism of diffusive creep-cavity growth in metals at elevated temperatures, which is the reverse of the mechanism of sintering. In the case of creep, atoms from the surface of the grain-boundary cavity are induced to diffuse into the surrounding grain boundary by the effect of a tensile stress normal to the boundary. When an atom leaves the surface and enters the boundary, the stress does work equal to the stress times the atomic volume; this is the gradient in chemical potential that drive the diffusion. The only difference in the case of dynamic embrittlement is that the diffusing atom is a surface-adsorbed embrittling element, usually a low-melting element that is more mobile than the matrix elements, as indicated schematically in Fig. 4.

Fig. 4 Schematic representation of the atomic process involved in dynamic embrittlement.



There are two forms of dynamic embrittlement. In one, the embrittling element comes from surface segregation in the alloy itself, starting at an internal grain-boundary cavity produced by deformation. This is the case with stress-relief cracking in steels, which is caused by sulfur [7-9]. Another example is found in Cu-Sn alloys, in which the embrittling element is tin; the process in the Cu-Sn alloys is analogous to the cracking in steels [10]. In the case of the steels, the sulfur is liberated from sulfides by the high-temperature excursion that occurs in the heat-affected zone alongside a weldment, and the sulfur then segregates to grain boundaries upon cooling (and presumably precipitates as less-stable sulfides) [7,8]. The cracking starts below the surface in a high-stress region and propagates in bursts along fast-diffusion grain boundaries, leaving un-cracked ligaments in its wake. An example is shown in Fig. 5

(a) (b)

Fig. 5. (a) Variation of crack velocity with time in a steel specimen in which cracking by sulfur-induced dynamic embrittlement was interrupted. (b) Sketch of the fracture surface showing the un-cracked ligaments (grey) and the cracked area (white) as cracking percolated along fast-diffusion grain boundaries. The grey regions are low-temperature cleavage that occurred in impact after the specimen was unloaded and cooled. The cross-hatched region is the pre-crack. Ref. 8.

Another form of dynamic embrittlement is induced by elements in the surrounding atmosphere, and the type that has received the most attention is that of oxygen-induced cracking. It has been studied in a nickel aluminide [11], in a Cu-Be alloy [12], and in nickel-base superalloys, especially IN718 [13]. The latter case is found in so-called “hold-time cracking” of components of gas-turbine engines when cyclic loading is interspersed with sustained periods of high stress. Pfaendtner has studied this phenomenon by static fixed-displacement loading of IN718 in pure bending at 650°C [13] and has found that the cracking is essentially similar to that found in the other cases of dynamic embrittlement mentioned above. The cracking kinetics were studied in various oxygen pressures, as shown in Fig. 6. The velocity vs. stress-intensity curves were calculated from the load vs. time curves with the aid of a compliance calibration of the specimen.

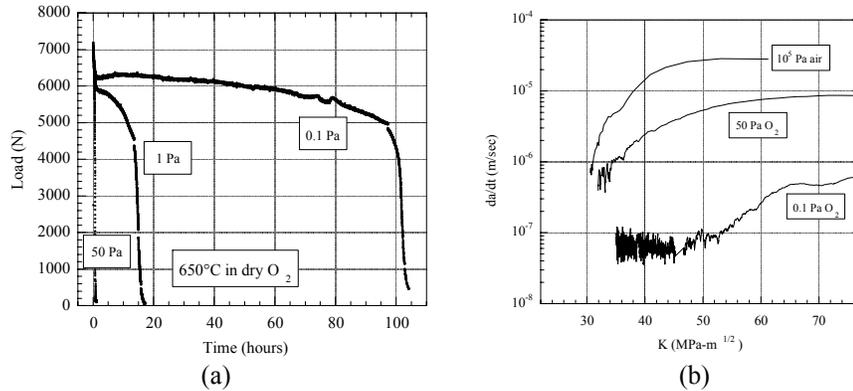
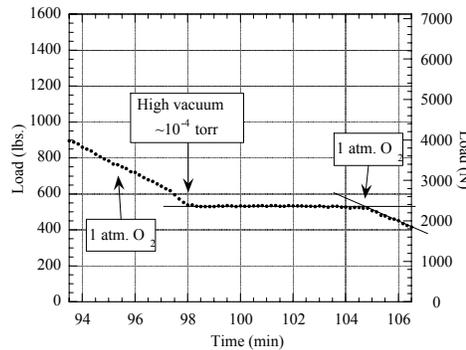


Fig. 6. (a) Examples of load-relaxation curves due to intergranular cracking of notched pure-bend specimens of IN718 held at fixed displacement at 650°C in several pressures of oxygen. (b) Curves of crack velocity vs. stress intensity calculated from such load vs. time curves. Ref. 13.

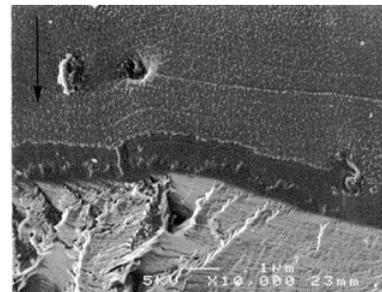
Pfaendtner found that the cracking could be stopped and re-started by switching from oxygen to vacuum in his test chamber and then back again to oxygen, as illustrated by Fig. 7. Because the changeovers occurred in a matter of seconds, it was clear that the embrittlement-process zone had to be very close to the crack tip and that long-range diffusion of oxygen into the specimen could not be a factor.

Fig. 7. Enlarged view of the arrest in the load vs. time curve for an IN719 specimen cracking in oxygen at 650°C that occurred when the oxygen was pumped out of the test chamber. The cracking restarted as soon as oxygen was re-admitted. Ref. 13.



One common characteristic of dynamic embrittlement in polycrystals is that it occurs discontinuously. This can be seen clearly on the fracture surfaces of the IN718 cracked in oxygen, because the crack-arrest lines are marked by oxide that forms during the arrest. An example in a specimen that had been partially cracked in oxygen and then unloaded, cooled, and broken open at a low temperature is shown in Fig. 8. The dark band at the end of the intergranular (high-temperature) cracking presumably is the result of the closing of the crack tip during the unloading, so that less oxide was formed behind the crack front. At this point the crack had been traveling at a rate greater than 10 μm/sec, so the 1-μm-wide band must have formed in less than 0.1 sec. There are five arrest marks seen faintly inside the band, so the crack was moving forward by about 0.2 μm every 0.02 sec. (Note that oxygen penetration over this entire distance in this time would have required a diffusion coefficient of about 10⁻⁸ cm²/sec, which is impossibly high. This emphasizes further that the diffusion of oxygen occurs on a much finer scale.)

Fig. 8 Example of crack-arrest marks in a specimen of IN718 that was partially cracked in oxygen at 650°C before being unloaded and broken open at a low temperature. See text. Ref.13.



The reason for the discontinuous cracking in polycrystals is

that, because of the dependence of the diffusion rate on grain boundary structure, at any instant the crack is moving forward at only some specific locations. The load is being carried by the parts of the specimen that are not cracking at that instant, which explains why the stress intensities are so high (cf. Fig. 6b) in spite of the fact that this is a sharp-crack kind of fracture. Every time the crack front jumps forward at any given location; the local stress drops; power-law creep then occurs in that region, and the crack is re-loaded for the next jump. This is why the apparent activation energy for this cracking is that of power-law creep (i.e., self-diffusion). For this reason, one cannot do a more fundamental study of this phenomenon using polycrystals. Rather, bicrystals, in which this kind of constraint is absent, are necessary to study the dependence of the cracking rate on temperature and stress intensity. It has been found that cracking by dynamic embrittlement in bicrystals of Cu-Sn [14] and IN718 [15] is continuous and that it occurs at stress intensities of only a few $\text{MPa}\sqrt{\text{m}}$.

4. ACKNOWLEDGEMENT

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5. REFERENCES

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