

SLOW BRITTLE FRACTURE

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ABSTRACT

In contrast to the catastrophic types of brittle fracture in which cracks propagate unstably at hundreds of meters per second, brittle fracture can occur in a stable fashion at speeds that are many orders of magnitude slower. This occurs as a result of surface contamination by a mobile embrittling element that is induced to diffuse into a solid, usually along grain boundaries, under the influence of an applied stress. Examples are common in various engineering structures, but it is not widely recognized that they all belong to the same generic form of brittle fracture.

KEY WORDS: dynamic embrittlement, brittle fracture, intergranular fracture

INTRODUCTION

The term “brittle” is used here to denote fracture by decohesion that occurs apart from any plastic process. That is, plasticity may occur concomitantly, but it is not an essential part of the decohesion process. In the familiar fast brittle fracture in metals by transcrystalline cleavage or intergranular decohesion, plasticity is usually essential to crack nucleation, but is only incidental to crack propagation. The same applies here to slow brittle fracture.

Slow brittle fracture involves the propagation of a crack in a solid the surface of which is contaminated by an element that, when concentrated in the solid, would reduce the local cohesive strength. The application of a tensile stress to a solid in which a crack has nucleated both stretches bonds and causes the embrittling element to diffuse inward at the tip of the crack. This allows the crack to spread at a rate dependent upon the rate of diffusion of the embrittling element from the surface into the region ahead of the crack tip. This process has been termed “dynamic embrittlement” [1,2].

The phenomenon of dynamic embrittlement can be categorized according to the available concentration of embrittling element at the crack tip. The three categories being studied systematically in alloys are the following:

- (i) Low concentration. The embrittling element comes by way of surface segregation from the alloy itself.

(ii) Moderate concentration. The element comes from the vapor phase around the alloy.

(iii) High concentration. The embrittling species is in a liquid phase.

EMBRITTEMENT FROM SURFACE SEGREGATION

The phenomenon was first recognized in the context of stress-relief cracking of alloy steels [3]. This is sometimes found in the coarse-grained heat-affected zone of welds, usually in thick sections. During the welding process, the HAZ reaches temperatures high enough to allow some dissolution of sulfides in the steel. During cooling, the dissolved sulfur segregates to austenite grain boundaries and then re-precipitates as very fine (probably metastable) sulfides in these boundaries. When the structure is later heated to allow relief of the residual stresses by creep, cavities can nucleate around large intergranular particles, like oxides or sulfides. If the stress is high enough, brittle cracks can grow from these cavities. This is caused by the presence of elemental sulfur that is segregated on the surfaces of the cavity and the subsequent crack and is then induced to diffuse into the grain boundary ahead of the crack by the tensile stress normal to the grain boundary, as illustrated schematically in Fig. 1. Sulfur is a very potent embrittling element in iron, and the concentration needed for decohesion at the stresses involved is probably less than one atom in ten [21].

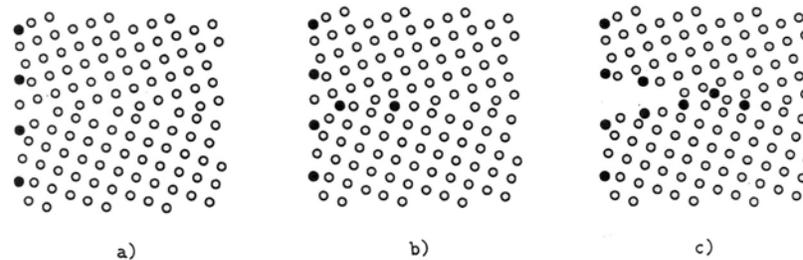


Fig. 1 Schematic representation of (a) surface adsorption of an embrittling element, (b) inward diffusion driven by a tensile stress, (c) decohesion in the diffusion zone.

The process depicted in Fig. 1 is analogous to the classical Hull-Rimmer mechanism of diffusive growth of creep cavities [4], which is the reverse of the sintering process. The stress across the grain boundary provides a gradient in chemical potential of atoms on the surface *vs.* in the bulk solid. That is, the stress does work when surface atoms diffuse into the bulk in exchange for lattice vacancies. Unlike in creep-cavity growth where the diffusing atoms are the same as in the bulk, in dynamic embrittlement the surface atoms are a mobile (i.e., low-melting) element that is adsorbed on the cavity/crack surface.

In a detailed study of stress-relief cracking using a simulated HAZ in a NiCrMnMo steel cooled rapidly from a high temperature [1], the following characteristics were found:

(i) The initial crack growth is macroscopically discontinuous, occurring in bursts, as indicated by the results from a compact-tension specimen under a constant load at

550°C in vacuum, as shown in Fig. 2. Fractography by SEM showed that each burst represented cracking of a number of grain boundaries.

(ii) The local rate of crack advance is highly variable, depending on the grain-boundary structure, which determines the rate of diffusion of the surface element into the boundary. This results in a highly irregular crack front and in slow-cracking ligaments left behind the main crack front.

(iii) The tip of the growing crack is so sharp that no appearance of blunting could be found by examination of the fracture surface at the highest available resolution in the scanning electron microscope.

To test the hypothesis that this is a generic form of brittle fracture, similar experiments were carried out on a Cu-8%Sn alloy (without the prior high-temperature treatment). Compact-tension specimens loaded at 265°C in vacuum exhibited behavior essentially similar to the steel [5], including intergranular decohesion and cracking in bursts. In this model material the tin played the role of sulfur in the steel. It is surface active [6], and it is a low-melting embrittling element in steel [7]. The conclusion is that the low creep ductility [8] and the hot shortness [9] exhibited by Cu-Sn alloys are both analogous to stress-relief cracking in steels.

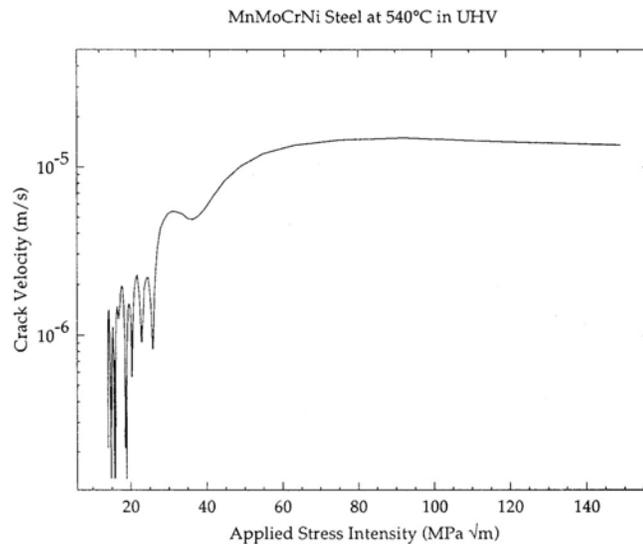


Fig. 2 Example of crack growth in bursts in the early stages of sulfur-induced dynamic embrittlement (stress-relief cracking) [1].

To test the idea that dynamic embrittlement requires diffusive penetration of the solid, which depends on the grain-boundary diffusion rate and thus grain-boundary structure, experiments were done on Cu-Sn bicrystals [10]. In specimens with $\Sigma=5$ (031)[100] symmetrical tilt boundaries made by diffusion bonding and loaded in vacuum at 265°C, it was found that a crack could be grown easily along the tilt axis, but not transverse to the tilt axis. This corresponds to cracking along the fast-diffusion direction but not the slow-diffusion direction.

In the initial set of experiments, the boundaries had a residue of sub-micron-size alumina particles from metallographic polishing. Later, specimens were prepared without this residue [10], and still later by growth from the melt, also without particles [11]. The boundaries in this set of specimens were found to be difficult to crack, even along the fast-diffusion direction. Two conclusions were drawn from this. The first is that dynamic embrittlement may well follow the pattern of other types of grain-boundary failure [12-14] in which boundaries with Σ -value less than about 29 are particularly resistant to failure. The second conclusion is that the presence of particles probably enhanced the surface concentration of tin by decohering ahead of the crack and allowing tin to segregate to the new surfaces thereby created. They would thus have served a role analogous to that of the small sulfides in the steel. The influence of grain-boundary particles is an area that deserves further study.

EMBRITTLEMENT FROM THE ENVIRONMENT

Motivated by reports of oxygen-induced intergranular cracking in Cu-0.25%Be [15] and in nickel-base alloys, particularly alloy 718 [16], experiments were carried out to see if these types of cracking were analogous to the phenomena described above. When the steel and the Cu-Sn alloy were loaded at fixed displacement as notched bars in vacuum at elevated temperatures and the Cu-Be and alloy 718 were loaded similarly in oxygen, essentially the same behavior was found in all cases. The crack velocity could be calculated from the load-relaxation curve and the relation between specimen compliance and crack length. An example of the effect of oxygen pressure is given in Fig. 3.

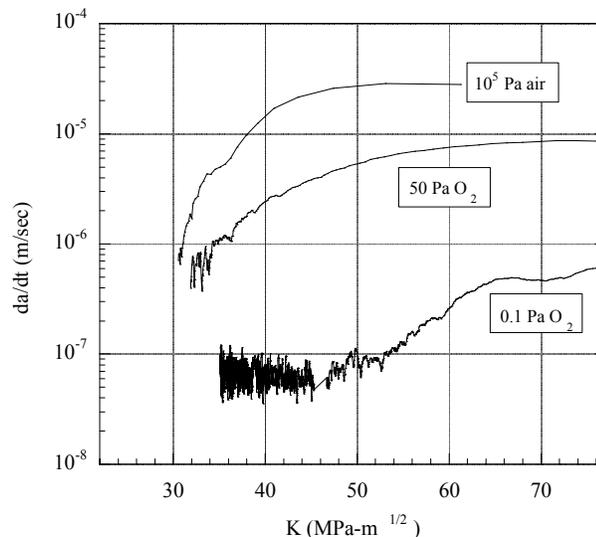


Fig. 3 Crack velocity vs. stress intensity curves derived from the load-relaxation curves and the compliance-calibration curve for alloy 718 at 650°C in various pressures of oxygen [17].

Examination [17] of the fracture surfaces of the alloy 718 showed the typical decohesion appearance when the oxygen pressure was high enough. However, at very low pressures the growth rate dropped by several orders of magnitude, and the fracture appearance changed to a series of striations marked by strings of oxide, indicating that the cracking occurred in jumps at time intervals long enough for significant oxidation at the crack tip. The cracking at

higher oxygen pressures was also discontinuous (on the sub-micron scale), but the time intervals were much shorter, and the crack remained essentially sharp. Similar crack-arrest marks have been seen in all cases of dynamic embrittlement in polycrystalline specimens, but the cracking of the Cu-Sn bicrystals was continuous [10].

Our interpretation [17] of the fracture-surface observations was as follows: Cracking in polycrystals at sufficiently high surface concentration of the embrittling element occurs by the advance of sharp intergranular cracks caused by oxygen-induced decohesion, but at different rates along the crack front, depending on the local grain-boundary diffusivity. At any instant the main crack is advancing in some places, but not in others, and the load is therefore carried by the non-cracking regions. This shields the cracking regions from stress and allows the existence of sharp crack fronts. However, at any region of cracking the local stress relaxes as the crack moves forward, and the crack then has to stop and wait for creep of the non-cracking regions to raise the stress again. Thus, the cracking of a polycrystal is discontinuous because of the constraint imposed by non-cracking regions at any moment in time. The result is that large stress intensities are borne by the specimen (Fig. 3), but this does not reflect the stress intensity at the points of sharp-crack advance. In addition, the temperature dependence of cracking is found [17] to be consistent with that of self-diffusion in the alloy, rather than with the intergranular diffusion of the embrittling element in from the surface, because the cracking is constrained by the rate of power-law creep in the non-cracking regions.

Continuing this interpretation, in the case of cracking at very low oxygen pressures, oxygen atoms arrive at the crack tip so slowly that they have time to diffuse away along the grain boundary, down the gradient of chemical potential provided by the local stress. The crack then has time to blunt, and the oxygen collects in the region of maximum stress ahead of the blunt crack. When the concentration becomes high enough, cracking occurs back to the crack tip, and the process is repeated.

Oxygen-induced cracking in nickel-base alloys has been studied mainly in the context of cyclic loading and the effects of hold-time and loading rate on intergranular fatigue-crack growth [16,18]. The results obtained under fixed displacement conditions [17] indicate that the cyclic nature of the loading in the previous studies is incidental to the crack-growth process.

Experiments to study cracking in liquid metals using the same fixed-displacement, load-relaxation approach as outlined above have been only partly successful. It has been found with mercury and several copper-base alloys that the cracking is either too rapid to control or is so slow that it has to be driven with a moving cross head on the testing machine [19,20]. Much more work is needed in this area.

SUMMARY

It is now evident that dynamic embrittlement is a generic form of brittle fracture that involves decohesion caused by the inward diffusion of surface-adsorbed embrittling

elements, driven by an applied tensile stress. The source of the embrittling element can be the alloy itself (e.g., sulfur in steel and tin in Cu-Sn alloys) or the surrounding environment (e.g., oxygen in Cu-Be or in nickel-base alloys). Liquid-metal-induced cracking is thought to be a form of dynamic embrittlement, but this has not yet been demonstrated satisfactorily.

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