

Fig. 1. Differential shrinkage of oven-dried sample due to unequal stress distribution. Specimen on left subjected to incremental loading $\Delta p/p = 1$; specimen on right tested by a continuous load increase technique

loading tests (pore water pressure assumed to be zero) a more uniform consolidation is visualized. This appears to have an important effect on the measured preconsolidation pressure. Although the phenomenon reported was observed in a highly compressible, sensitive clay it may be found in other soils.

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METALLURGY

Interstitials and Fracture of Metals

INTERSTITIAL alloying elements, even in minute quantities, exert a potent influence on the mechanical behaviour of alloys. Of particular recent interest has been the behaviour of hydrogen in steels; where the phenomenon of hydrogen-induced delayed brittle failure has received special attention¹⁻⁹. Time-dependent brittle failure implies that spontaneous brittle fracture will occur at loads substantially below those that may have been previously successfully sustained. The characteristic features are: (a) an incubation period; (b) slow crack propagation; (c) a lower critical stress below which failure will not occur. Both the incubation period for crack initiation and crack growth are controlled and paced by the diffusion of hydrogen^{4-6,8}.

The incubation period depends on the time required to accumulate a critical concentration of hydrogen in the region of maximum triaxiality. Diffusion to this region is induced by the strain gradient associated with the inhomogeneous stress field, wherein the strain gradient acts as an activity gradient or driving force. It has been demonstrated recently⁹ that the attainment of the critical hydrogen concentration is determined by the magnitude of the applied stress. That is, the applied stress governs the magnitude of the strain gradient. High triaxial stress states are brought about by notches. The notches may be artificial (excavated), inherent (inclusions, grain boundary intersections, dislocation arrays, etc.) or combinations of these. However, when brittle fracture is involved, modern theory requires one of the effective notches to be a dislocation array. Therefore, coupled with the strain gradient of an artificial notch may be an additional driving force associated with a dislocation

array at the base of the notch. All this suggests that there are two criteria for delayed brittle failure; specifically, a critical concentration of hydrogen and a critical stress state. These two criteria are the basis of the discontinuous nature of crack propagation which is a unique characteristic of this type of time-dependent brittle failure.

The occurrence of discontinuous crack propagation makes it difficult to rationalize delayed brittle failure by applying any mechanism which postulates raising the flow stress to the fracture strength. On the other hand, a decrease in the cohesive strength of the lattice provides a ready explanation for this phenomenon. This could be brought about by localized concentration of interstitial atoms in the region of the critical stress state in the form of an uncondensed atmosphere¹⁰. Probably a more general situation would be one which involves both a rise in flow stress brought about by plastic deformation and a lowering of the cohesive strength. Presumably the proportions of these two could vary over a wide range.

Once the crack has been initiated, it will be propagated until it exceeds the radius of influence of the accumulated interstitials. Beyond this point the moving crack will be damped out rapidly due to plastic flow ahead of the crack. Another incubation period is then required to build up the critical concentration at the tip of the crack. This step-like process continues until the effective area is reduced such that the applied stress is equal to the notched strength of the material. Thus, a lion's share of the time to failure resides in the sum of the successive incubation periods.

No restrictions are apparent which limit this behaviour to hydrogen and steel. Indeed, the only restrictions to a general behaviour of this type are that a critical stress state exists and that the interstitials have sufficient mobility to attain a critical concentration in a reasonable length of time. Hence, one may well anticipate that any interstitial in any metal which can accommodate the critical stress state may induce delayed brittle failure.

A major step in evaluating this concept involved an examination of the particular case of carbon (nitrogen) in steel. In the temperature-range 700–1,000° F. carbon has approximately the same mobility

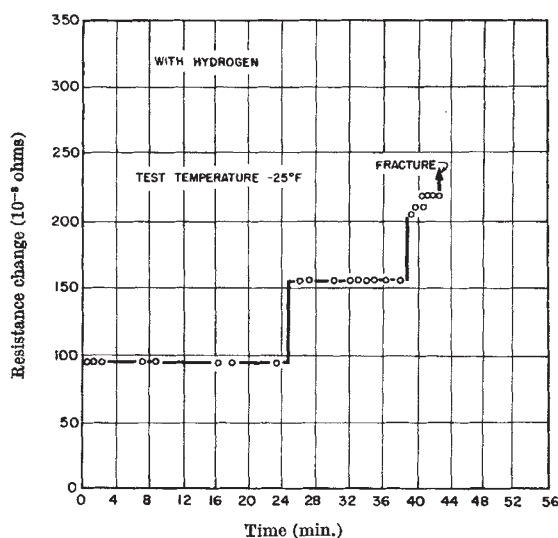


Fig. 1. Resistance vs. time in the delayed-failure stress range of a uniformly hydrogenated nickel-chromium-molybdenum steel

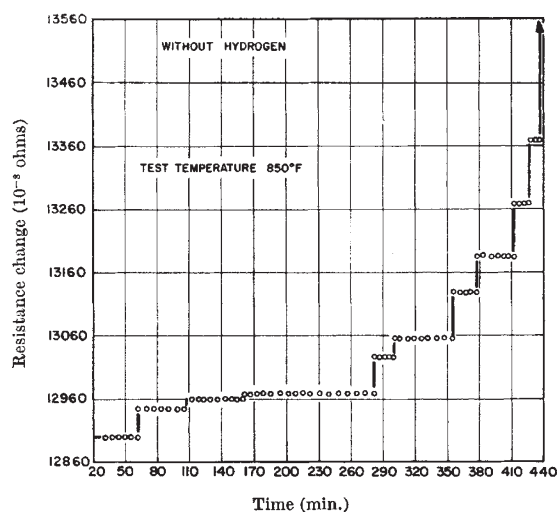


Fig. 2. Resistance vs. time in the delayed-failure stress range of a high-temperature die steel

in steel as has hydrogen at room temperature. Notched specimens of a high-temperature die steel (0.40 per cent carbon, 0.35 per cent manganese, 1.10 per cent silicon, 5.00 per cent chromium, 0.90 per cent vanadium, 1.35 per cent molybdenum) were subject to sustained-load-to-failure tests in the appropriate temperature-range. Resistance versus time measurements^{3,4} were recorded during the sustained-load tests. All the significant features of time-dependent brittle failure were observed in an almost perfect image of the behaviour of hydrogen in steel (cf. Figs. 1 and 2). Fig. 2 vividly illustrates the incubation period and the step-like appearance associated with discontinuous crack propagation.

These results lend authority to the concept that interstitial-induced delayed brittle failure may be a general behaviour in metals which can attain the critical stress state in the temperature-range dictated by the mobility requirement. The implications derived from this work are far-reaching. They indicate that 'pressure in a void' is unnecessary to explain time-dependent brittle failure. In addition, they suggest the possibility of unifying this behaviour with other, more familiar, phenomena which also are paced by the diffusion of interstitials, such as slow-strain-rate embrittlement and strain ageing¹⁰.

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Determination of Oxygen in Iron and Steel

WE have recently applied the method of stable isotope dilution¹ to the determination of oxygen in samples of iron and steel which contained low concentrations of this element. As our results are consistently higher than values obtained by the conventional vacuum-fusion method, this preliminary account of our work is submitted.

The technique consists of allowing the steel sample to react with carbon at 1,500° C. in an atmosphere containing a known amount of carbon monoxide enriched in the isotope oxygen-18. Measurement of the ratio $R = {}^{18}\text{O}/{}^{16}\text{O}$ in a sample of the gas after equilibration enables the oxygen content of the metal to be determined. 'Blank' corrections are negligible, but as an additional precaution may be avoided by prior equilibration of the graphite crucible used as container for the sample in an atmosphere containing the same relative amounts of oxygen-18 and oxygen-16 as the expected final equilibrium value R .

Various methods have been used to determine the ratio R . At first, use was made of the mass spectrometer ion currents at $m/e = 30$ and 28 due to singly ionized C^{18}O and C^{16}O respectively. Here, however, it is necessary to apply a correction, based on the ion current at $m/e = 14$, to the value at $m/e = 28$, because nitrogen from the steel is always present in the gas mixture at the end of a dilution. A more accurate method is to convert part of the carbon monoxide in the equilibrated gas mixture to carbon dioxide, and to measure the ion currents at $m/e = 44$, 46 and 48. The value of R is then given by either $2h_{48}/h_{46}$ or by $(h_{48}/h_{44})^2$, where h_x represents the ion current at $m/e = x$. The three methods yield results which agree within experimental error. Instrumental errors are avoided by using the same method for both calibration and analysis.

Calibration is effected by admitting to the furnace small measured quantities of normal and enriched oxygen in proportions similar to those encountered in an analysis. Conversion of carbon monoxide to dioxide without isotopic dilution is achieved by compressing part of the gas mixture from the furnace into a small circulatory system which contains a platinum filament heated to 900° C. and a trap cooled in liquid air. By this means the equilibrium:



is constantly displaced until sufficient carbon dioxide has been formed for analysis.

Table 1 summarizes the calibration and analytical results for a standard steel sample, designated BPL-21, supplied by the British Iron and Steel Research Association. The mean oxygen content of this steel as determined by several independent investigators with the vacuum-fusion method is given as 0.003 per cent, with an overall range of 0.002–0.004 per cent for individual determinations. Our values are thus higher by a factor of about two. The scatter between individual analyses is not improved.

It is estimated that the combined sources of error in the above analyses should not exceed ± 25 per cent for any single determination. In the analysis of several iron-carbon alloys prepared in this laboratory, results have been duplicated to within 10 per cent in the range 0.006–0.011 per cent oxygen. These figures were again higher than the corresponding vacuum-fusion results by a factor of two to four. The good reproducibility obtained with specimens