JOURNAL OF MATERIALS SCIENCE 14 (1979) 2563–2566

The embrittling effects of hydrogen on a variety of inorganic materials as indicated by acoustic emission

R. E. CUTHRELL, E. RANDICH
Sandia Laboratories, Albuquerque, New Mexico 87185, USA

The embrittling effects of hydrogen-bearing environments which were previously shown in detail for a few selected materials, are reported here for a wide variety of inorganic solids including glasses, ceramics, single crystal minerals, rocks, refractory coatings, semiconductors, and metals. Prior work showed the hydrogen effect using several quite different techniques and environments. The measurements for the present survey were restricted to acoustic emission amplitude distributions during drilling under carbon tetrachloride (a hydrogen-free liquid environment) and under water (a source of hydrogen). It is proposed that the hydrogen effect is a universal phenomenon which affects the deformation and fracture behaviour of solids (organic materials may be exceptions).

1. Introduction

Rebinder demonstrated that adsorbed surface-active species could affect the microhardness of certain minerals [1]. These and other manifestations of the effects of chemical environments on mechanical behaviour are often termed Rebinder effects.

The influence of several chemical environments on the microhardness of a large number of ionic and ceramic crystals was investigated by Westbrook and Jorgensen [2], following earlier work by Mitsche and Onitsch [3] and Walker and Demer [4]. The anelastic behaviour of glass fibres [5, 6], the Vickers microhardness and indentation creep of fused silica and alkali glass [7], the pendulum hardness of soda-lime glass [8, 9] and quartz [10], and the drilling rates in calcium fluoride [11], magnesium oxide [11], Pyrex glass [12], soda-lime glass [9], aluminium oxide [13], grey granite [13], and Westerly granite [13], are all known to be strongly dependent on the chemical environment. A very significant contribution to understanding these Rebinder effects was made by Westwood and Macmillan [13], on interpreting the correlation between the maximum in the hardness of materials and the zero in the surface charge (zeta potential) which is produced by ions adsorbed from solution environments.

Using acoustic emission to monitor the low-speed drilling or grinding of solids, it was recently shown that minimum emission rates (minimum wear rates) were associated not only with the zero zeta potential, but also with the drilling fluid dielectric constant for which ions in solution were bound together as ion pairs [14]. It was proposed that an embrittling effect due to the presence of hydrogen was responsible for the Rebinder–Westwood chemomechanical effects and that, for hydrogen-bearing drilling fluids, hydrogen ions were least available for embrittlement when maximum pairing of ions occurred. This theory was given substance by the results of drilling experiments in ultrahigh vacuum ($\sim 5 \times 10^{-10}$ Torr), in gaseous hydrogen in the vacuum chamber (680 Torr ultrapure hydrogen was assured by equilibrating the gas with a thick layer of freshly sublimed titanium), under hydrogen-free liquids (carbon tetrachloride and trifluorotrichloroethane), and under liquids of progressively greater hydrogen availability (dimethylpolysiloxane, a non-ionizing liquid from which hydrogen may be made available only by the catalytic cracking of covalent bonds

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at the freshly machined surfaces and in which the availability is further limited by slow diffusion of reactancts as a result of high fluid viscosity, 100 cP; dichloroethane, a low viscosity liquid in which hydrogen is covalently bound; ethanol, a liquid in which hydrogen ions are available in very limited amounts as a result of a very low auto-ionization constant of about 10^{-20}; and water, a liquid in which hydrogen ions are readily available as a result of an auto-ionization constant of 10^{-14}) [15, 16]. These results suggested that the availability of hydrogen for embrittlement depends on its bonding in the drilling fluid (covalent, ionic, or ion paired in media of low dielectric constant) and on the viscosity of the fluid.

The present survey was undertaken to determine if the hydrogen embrittlement effects as discussed above were exhibited by other materials. Results are presented here for a wide variety of ionorganic materials including glasses, ceramics, single crystal minerals, rocks, refractory coatings, semiconductors, and metals. It must be noted that the precise mechanism of embrittlement in these materials is not yet well understood. The purpose of the study is to show that the effect does exist in many solids.

2. Experimental details

Holes were drilled in samples (2.54 cm diameter x 0.318 cm thick) with a 3 mm spherical ended diamond-studded bit rotated at 10 r.p.m. under a normal load of 1500 g and various drilling environments. It should be noted that drilling at 10 r.p.m., which was chosen to avoid heating effects, may be more closely related to low velocity abrasive wear tests that to conventional drilling at high speeds. Drilling environments included water, carbon tetrachloride, and ultrahigh vacuum. Prior to each drilling experiment, the samples were ultrasonically cleaned in trichloroethylene and acetone. The acoustic emissions accompanying the fracture of the samples during drilling were filtered and monitored using equipment described previously [14]. Acoustic emission amplitudes, which were found to be proportional to the drilling rates [16], were measured over a 60 dB range.

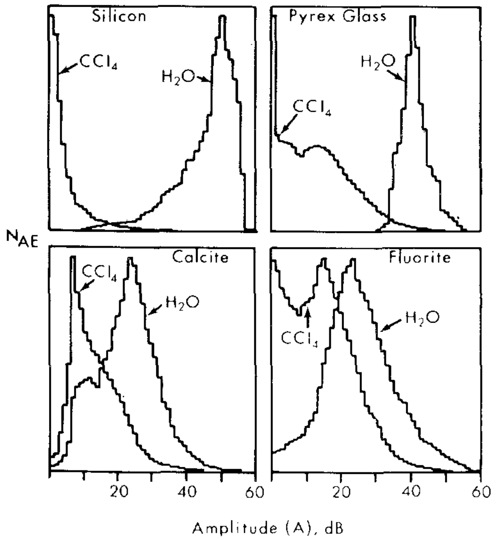

Figure 1 Acoustic emission amplitude distributions for the drilling of the indicated solids under carbon tetrachloride (a hydrogen-free liquid) and under water (a source of hydrogen). Scanning electron microscopy showed that silicon fractured in a ductile manner under the former and in a brittle manner under the latter liquid [16].

3. Results and discussion

Prior drilling results [16] showed that peaked acoustic emission amplitude curves such as shown in Fig. 1 for silicon were associated with the fracture of brittle materials such as glasses, ceramics, refractory compounds, etc. Curves monotonically decreasing to the abscissa, on the other hand, were associated with the fracture of ductile materials, i.e. metals (also shown in Fig. 1 for silicon). As an example, this brittle/ductile correlation was clearly demonstrated in the case of high-purity iron (Ferrovac E) when tested above and below its brittle-to-ductile transition temperature [16].

The environmental effect on drilling rates was found to produce progressively higher amplitudes for the peak acoustic emission (higher drilling rates) as the hydrogen availability for embrittlement of the solids was increased [15, 16]. This environmental effect was shown recently in slow crack-growth experiments as a trend toward lower stress intensity required for crack propagation with increasing hydrogen availability [17].

Since carbon tetrachloride and water represent two extremes in hydrogen availability from the drilling fluid, drilling alternately under these two liquids was performed in the present survey of inorganic materials. Drilling results for: silicon, Pyrex glass, calcite, fluorite (Fig. 1); synthetic quartz, fused silica, hot-pressed titanium diboride (Fig. 2); hot-pressed boron carbide (B_4C, not shown); sierra white granite (Fig. 2); Texas pink granite, fully hardened tool steel, spheroidized

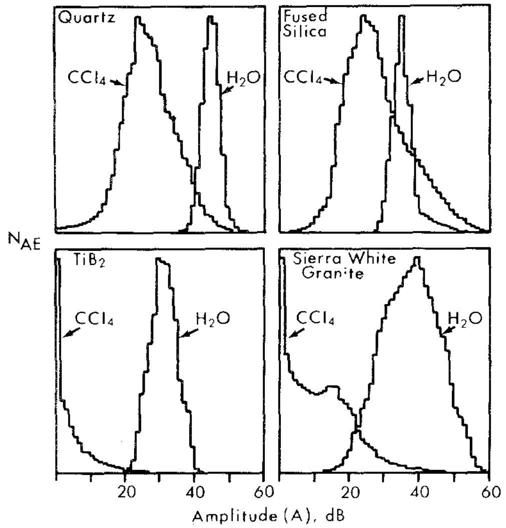

Figure 2 Acoustic emission amplitude distributions for the drilling of the indicated solids under carbon tetrachloride and under water. Peaks at lower amplitudes were associated with decreased embrittlement as a result of limiting the availability of hydrogen [16]. The drilling of hot-pressed boron carbide (B_4C) gave results which were similar to those for hot-pressed titanium diboride (TiB_2) shown above.

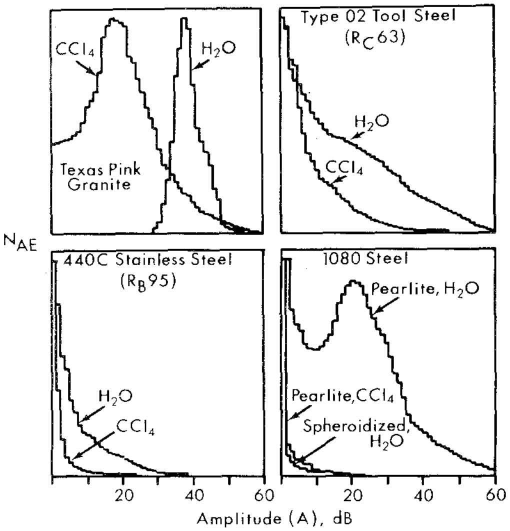

Figure 3 Acoustic emission amplitude distributions for the drilling of the indicated solids under protic (water) and aprotic (carbon tetrachloride) liquids. Note that distributions at higher amplitudes were obtained for the harder (Rockwell C 63) tool steel compared to the much softer (Rockwell B 95) 440C stainless steel in the spheroidized condition. The shift to lower amplitude for the pearlite (1080 eutectoid steel) on changing the drilling fluid from water to carbon tetrachloride indicates that the brittleness of the carbide platelets may be reduced by limiting the availability of hydrogen. The ductile behaviour of the spheroidized 1080 steel is consistent with fracture in the matrix surrounding the carbide particles.

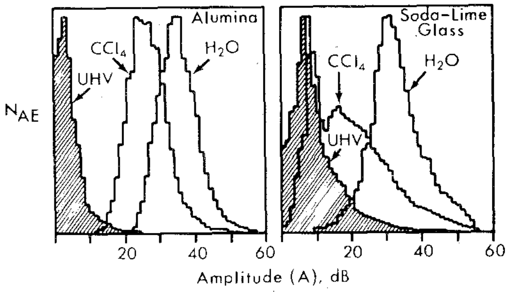

Figure 4 Acoustic emission amplitude distributions for the drilling of polycrystalline alumina and soda-lime glass in ultrahigh vacuum (UHV, shaded), under carbon tetrachloride, and under water. The intermediate amplitudes for drilling under carbon tetrachloride may be results of moisture trapped in the near-surface regions of the solids.

440C stainless steel [18] and 1080 steel (Fig. 3), consistently show lower acoustic emission amplitude distributions when drilled under carbon tetrachloride (a hydrogen-free liquid) and higher amplitude distributions when drilled under water (a source of hydrogen).

It should be realized, however, that although immersion of the sample in carbon tetrachloride may effectively minimize external sources of hydrogen, it does not allow hydrogen or hydrogen-containing adsorbates to degas from the sample surface, interior, cracks, or open pores as effectively as does bakeout in an ultrahigh vacuum system. Therefore, a reduction in embrittlement (a shift to lower amplitude of the acoustic emission peak) would be expected for changing the drilling fluid from water to carbon tetrachloride and a further reduction would be expected in some materials for drilling *in vacuo.* These expected results were obtained for the drilling of polycrystalline alumina and for soda-lime glass (Fig. 4). For the polycrystalline alumina, the relatively small shift of the acoustic emission peak to lower amplitude on changing the drilling fluid from water to carbon tetrachloride may be a result of the trapping of moisture on the surface and in the cracks, crevices, and open pores of the sintered solid in addition to the trapping of hydrogen in the interior. The much larger shift for drilling in ultrahigh vacuum (UHV) after bakeout is consistent with this interpretation. The relatively larger effect of carbon tetrachloride in the case of soda-lime glass, when compared with that of alumina (Fig. 4), is consistent with a reduced number of trapping mechanisms (surface-adsorbed moisture and interior hydrogen only — no cracks, crevices, or pores).

Acoustic emission amplitude distributions which decrease monotonically to the abscissa were associated with the fracture of ductile materials [16]. Ductile behaviour is indicated in Fig. 3 for the drilling of fully hardened type 02 tool steel and spheroidized 440C stainless steel. The microstructure of the tool steel consisted of Fe_3C particles in a matrix of untempered martensite while that of the 440C was Fe_3C particles in a ferrite matrix. The relatively broad acoustic emission amplitude distribution of the tool steel is interpreted as a result of the fracture of the hard martensite since the acoustic emission peaks previously associated with the fracture of a brittle phase (Fe_3C) are absent [16]. In comparison, fracture of the softer ferrite in the 440C results in an amplitude distribution of lower energy, i.e. further to the left. The data for type 02 tool steel and 440C stainless steel in Fig. 3 both show significant environmental dependence of the fracture processes.

The drilling of a 1080 (eutectoid) steel represents a unique test of the interpretation of the acoustic emission amplitude distributions. In the pearlitic condition it is impossible to drill an eutectoid steel without fracturing the brittle lamellar Fe_3C structure. In the spheroidized condition, however, the fracture path may easily pass through the ductile ferrite matrix and bypass most of the spherical carbide particles. As Fig. 3 shows, 1080 steel exhibits just such behaviour. In the spheroidized condition the 1080 steel behaves like spheroidized 440C (Fig. 3). However, when heat-treated to the pearlitic condition (medium pearlite), drilling the eutectoid under water produces a peaked acoustic emission amplitude distribution (indicating brittle behaviour), while drilling under carbon tetrachloride produces a "ductile" type curve. This change in behaviour is consistent with a marked decrease in brittleness of the carbide platelets as a result of drastically limiting the availability of hydrogen.

4. Conclusions

It is proposed that embrittlement by hydrogen is a universal effect (organic solids may be exceptions) since it has been shown in a wide variety of inorganic materials including ceramics, glasses, single crystal minerals, rocks, refractory coatings, semiconductors, and metals. Embrittlement by hydrogen may also be the origin of the Rebinder–Westwood chemomechanical effects. Since a variety of non-aqueous liquids produce embrittling effects which are intermediate between those of carbon tetrachloride and water and which appear to depend on the availability of hydrogen in each liquid [16], the environmental effects on slow crack growth of fatigue in brittle materials, which have been previously attributed to water [19], may be attributable to hydrogen from the water.

Acknowledgements

The authors thank D. M. Mattox for suggesting acoustic emission techniques for this investigation, and V. D. Nogle for sample preparation. This work was supported by the Division of Basic Energy Sciences, US Department of Energy (DOE), under Contract AT(29-1)-789.

References

1. P. A. REBINDER, Proceedings of the 6th Physics Conference, Moscow (1928).
2. J. H. WESTBROOK and P. J. JORGENSEN, *Trans. AIME* **233** (1965) 425.
3. R. MITSCHE and E. M. ONITSCH, *Mikroskopie* **3** (1957) 257.
4. W. W. WALKER and L. J. DEMER, *Trans. Met. Soc. AIME* **230** (1964) 613.
5. M. S. ASLANOVA, *C. R. Dokl. Acad. Sci. URSS* **95** (1954) 1215.
6. M. S. ASLANOVA and P. A. REBINDER, *ibid* **96** (1954) 299.
7. R. E. HANNEMAN and J. H. WESTBROOK, *Phil. Mag.* **18** (1968) 73.
8. A. R. C. WESTWOOD, G. H. PARR, Jr. and R. M. LATANISION, in "Amorphous Materials", edited by R. W. Douglas and B. Ellis (Wiley, London, 1972) p. 533.
9. A. R. C. WESTWOOD and R. D. HUNTINGTON, "Mechanical Behavior of Materials", Vol. IV (Soc. for Material Science, Japan, 1972) p. 383.
10. *Idem*, unpublished (1971).
11. A. R. C. WESTWOOD and D. L. GOLDHEIM, *J. Amer. Ceram. Soc.* **53** (1970) 142.
12. A. R. C. WESTWOOD and R. M. LATINISION, *Nat. Bur. Stand. (U.S.) Spec. Publ.* **348** (1972) 141.
13. A. R. C. WESTWOOD and N. H. MACMILLAN, in "The Science of Hardness Testing and Its Research Applications", edited by J. H. Westbrook and H. Conrad (ASM, Metals Park, Ohio, 1973) p. 377.
14. R. E. CUTHRELL, *J. Appl. Phys.* **49** (1978) 432.
15. *Idem, ibid* **49** (1978) 5676.
16. *Idem, J. Mater. Sci.* **14** (1979) 612.
17. R. H. MARION and R. E. CUTHRELL, unpublished (1979).
18. R. E. CUTHRELL, "Surface Effects in Crystal Plasticity", edited by R. M. Latinision and J. T. Fourie (Noordhoff, Leyden, 1977) p. 773.
19. S. M. WIEDERHORN, *J. Amer. Ceram. Soc.* **50** (1967) 407.

Received 29 December 1978 and accepted 28 March 1979.