

THE INFLUENCE OF CORROSION AND HYDROGEN CRACKING ON BLAST WEAR IN WET MEDIA

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Summary

Blast wear often occurs in the presence of an aqueous medium, thus raising the wear rate of most materials. At first sight, electrochemical dissolution seems to be important. However, the present paper shows that the mass loss due to dissolution (corrosion) is less than 2% of the total. In contrast, the mass loss significantly increases when the samples are charged with hydrogen before and/or during blasting. Thus we conclude that hydrogen cracking is the driving force in medium-promoted (blast) wear. Copper, as a very ductile material, is an interesting exception: diluted inorganic acids reduce the wear rate, obviously because of medium-dependent cold working.

1. Introduction

Many processes in coal power stations and chemical plants are characterized by a strong impingement of solid particles on materials ("blast wear") under wet conditions, *e.g.* in wet dusting. As proven by failure analysis and laboratory investigations [1, 2], wet media promote wear. This fact has not received much attention to date; most of the papers dealing with wear in general or blast wear in particular are confined to dry conditions.

2. Test device

The test device used for these investigations is shown in Fig. 1. As the details are given elsewhere [3-5], only a short description will follow (Table I). The suspension of the electrolyte and solid particles moves from the funnel into the central hole of the rotor. This rotor contains four channels in which the suspension

is accelerated by centrifugal force. The ratio of the solid particles to the fluid was adjusted to be less than or equal to 1:0.6. The essential data of the present paper are the mass losses estimated by gravimetry.

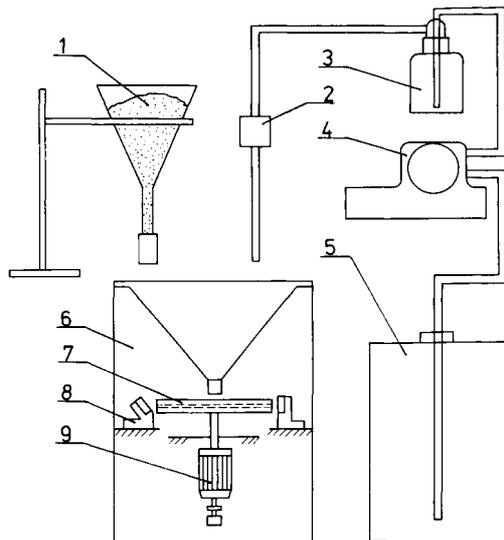


Fig. 1. Experimental apparatus for wear blasting: 1, abrasive container; 2, dosage of the fluid; 3, intermediate container; 4, pump; 5, storage of the fluid; 6, blast wear device; 7, rotor; 8, sample fastener with sample; 9, motor.

TABLE: 1

Conditions of the standard test (10 kg quartz sand 0.63, blast velocity 90 m s⁻¹)

Distance of the grains in the trajectory (mm)	5
Number of impacts per sample	10 ⁶ (total), 2000 grains s ⁻¹
Density of impacts (grains mm ⁻²)	7500
Stream angle 15°	25000
15°Stream angle 90	
Frequency of impacts (grains mm ⁻² s ⁻¹)	
Stream angle 15°	50
Stream angle 90	20

3. Electrochemical measurements

3.1. Methods and materials

During blasting, curves of current density vs. potential were plotted, associated with measurements of the corrosion potentials and corrosion currents. The corresponding circuit is shown in Fig. 2.

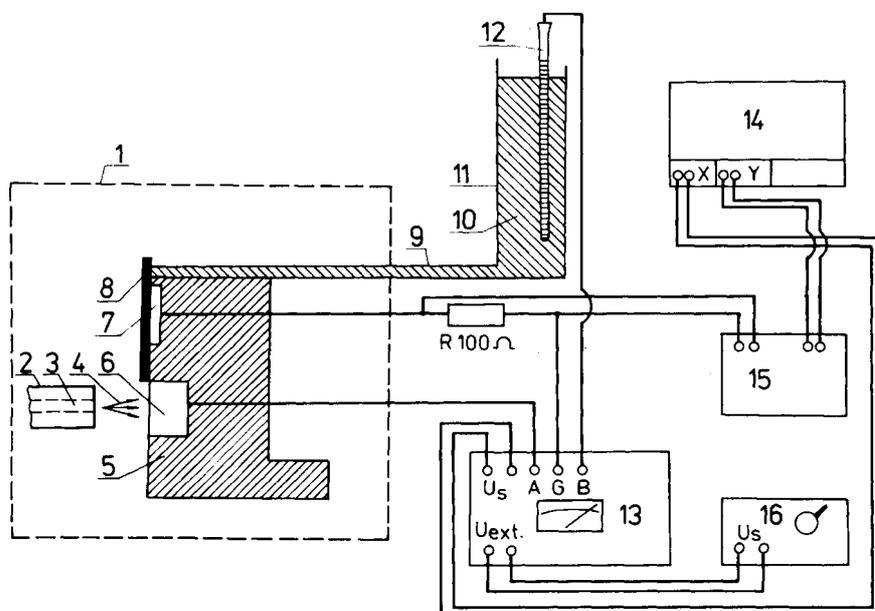


Fig. 2. Arrangement for electrochemical measurements: 1, blast wear device; 2, rotor; 3, blast channels; 4, suspension stream; 5, fastener for sample and counter electrode; 6, sample; 7, counter electrode; 8, cover (felt); 9, electrolyte bridge; 10, fluid; 11, intermediate container; 12, reference electrode (saturated calomel electrode); 13, potentiostat PS 3; 14, plotter; 15, algorithmic amplifier; 16, variator PV 2.

The samples (15 mm × 8 mm) were connected in the circuit, then embedded in epoxy resin, ground and fastened in the sample holder. The platinum counter electrode was attached above the sample and a felt cover protected it from the abrasive. The reference electrode, which is a saturated calomel electrode (SCE), was placed in a container arranged outside the blast device and was connected to the system by an electrolyte bridge. The curves of current density vs. potential shown here are confined to the anodic branch. The inclusion of the cathodic branch and the Tafel slope yielded the corrosion current which was almost equal to equilibrium. The corrosion current therefore represents the portion of mass loss due solely to dissolution. Electrochemical investigations were carried out on unalloyed steel St 38 and the high-alloyed stainless steel X8 CrNiTi 18.10 (AISI 304). The polarization of the first steel starts at -600 mV (SCE) and that of the second at -400 mV (SCE). The starting potential is about 50 - 100 mV more negative than the corrosion potential. A solution of 0.1 N H₂SO₄ with 0.1 N Na₂SO₄ was used as electrolyte. The latter compound was needed to improve the conductivity of the electrolyte bridge because of its great length. Quartz sand with a mean grain diameter of 0.63 mm served as the abrasive. The quantity of electrolyte added to the blast stream was 15 l h⁻¹. The velocity of the blast stream, *i.e.* the velocity of impact, was adjusted to range from 15 to 90 m s⁻¹. During blasting, the surface size of the samples steadily changes, thus yielding only an average value of the current density.

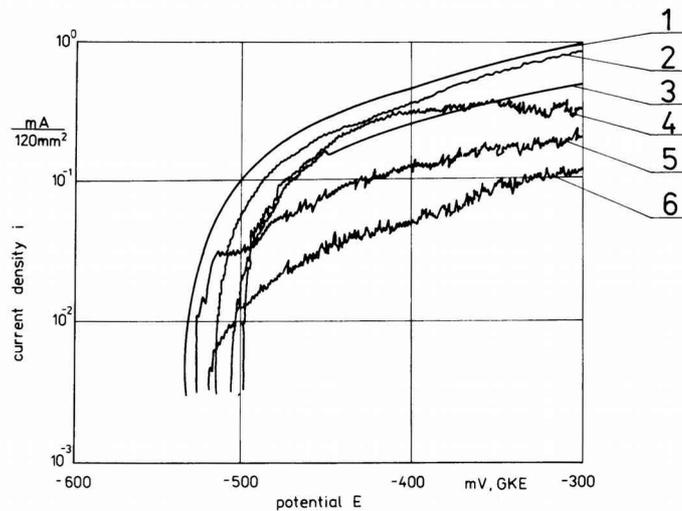


Fig. 3. Steel St 38 – curves of the current density vs. the potential taken during blast wear: abrasive, quartz sand (grain size less than 1 mm); electrolyte, 0.1 N H₂SO₄ + 0.1 N Na₂SO₄, 22 °C, pH 1.6; stream angle, 90°; start of polarization, -600 mV; rate of polarization, 20 mV min⁻¹. Curves: 1, steady state (electrolyte); 2, 30 m s⁻¹, electrolyte without sand; 3, 90 m s⁻¹, electrolyte without sand; 4, 30 m s⁻¹, sand suspension; 5, 60 m s⁻¹, sand suspension; 6, 90 m s⁻¹, sand suspension.

3.2. Results of electrochemical measurements

3.2.1. Unalloyed steel St 38

The curves of current density vs. potential under different conditions are presented in Fig. 3.

Without blasting, the current density continuously increases with the anodic potential. This tendency is typical of dissolution processes. For blast wear, however, the current density at a given potential decreases with increasing velocity of impact, *i.e.* the portion of mass loss due to dissolution decreases. When blasting occurred at a velocity as high as 90 m s⁻¹, the current density was ten times lower compared with static conditions. Further details are given in refs. 1 and 6. A (slight) decrease in the current density was also observed by Leitel *et al.* [7] using a rotating disc and a vibration device [8] for their studies on erosion corrosion. They explained this decrease in the current in terms of the formation of a mechanically induced reaction layer produced by the interaction of fresh surfaces of atomic size with the anions of the electrolyte. The wear conditions of their studies were rather weak (no information was given about the material loss) whereas our case of “sandblasting” revealed wear rates of 2 mm h⁻¹. Thus any kind of layer should already be destroyed in the initial stages.

In our study, the mass loss, which can be explained by electrochemical dissolution, is less than 2%, thus being negligible. This finding is supported by results of another study of Leitel *et al.* [9] carried out with a blast device similar to ours: the current density measured under different conditions was calculated as being 0.12% -1.6% of the medium-dependent part of the mass loss. However, it should be noted here that other authors investigating other kinds of wear have reported finding higher amounts of dissolution. In ref. 10 low-alloyed steel was worn with grinding paper immersed in 1% salt solution. At a potential of –

700 mV (SCE) the amount of dissolution was only 10% of the mass loss but at –400 mV (SCE) it was 54%, associated with an increase in the total mass loss. For sliding wear [11], too, the amount of dissolution was found to be about 50%.

In the present paper, the results of measuring the corrosion currents are shown in Table 2: no dependence on the experimental conditions is revealed. This is true also for the corrosion potentials when maintained in the narrow range 500 - 525 mV.

TABLE 2

Corrosion currents under various blast conditions

<i>Blast velocity</i> (m s ⁻¹)		<i>Corrosion current</i> (μA)
30	Sand–electrolyte	90
0	Steady state	80
30	Electrolyte without sand	70
90	Electrolyte without sand	62
90	Sand–electrolyte	55

3.2.2. *Stainless steel X8 CrNiTi 18.10*

The curves of current density vs. potential of this high-alloyed steel differ from those of unalloyed steel in the following two ways: the current density is enhanced by blasting; the current density does not depend on the intensity of blasting (*i.e.* impact velocity) whenever it occurs with sand suspension. Blasting with pure water revealed values which are nearly one order of magnitude smaller than those obtained with sand suspension and corresponds to static conditions. The water stream cannot damage the passive layer. The degree of damage to the passive layer by sand impact is too small for significant dissolution to proceed.

The measurement of corrosion currents revealed the same tendency: Blasting without sand yielded a corrosion current of only 3.5 μA. Blasting with sand suspension caused the corrosion current to increase up to 25 μA owing to slight but continuous damage to the passive layer. However, this value is still lower than that of unalloyed steel (55 - 90 μA) and also does not explain the medium-induced mass loss.

4. The influence of hydrogen on the wear rate

4.1. *The mechanism of hydrogen cracking*

Hydrogen, as the lightest element, has the smallest atomic diameter, nearly 0.1 nm. As a consequence, atomic hydrogen easily enters the metal lattice where it has a high mobility. This is especially true for ferritic steels owing to their b.c.c. lattice. In the more closely packed f.c.c. lattice of austenite (Cr-Ni) steels, the diffusion coefficient is nearly four orders of magnitude smaller than for

ferritic steels (*cf.* refs. 12 and 13) which generally results in a lower susceptibility to hydrogen cracking in the temperature range below 80 °C.

The nature of hydrogen cracking becomes most clearly visible in the case of so-called “fish eyes”, well known from welding samples [14, 15]. Starting from a large cavity (pore, slag inclusion, lack of fusion), a fine-structured crack zone is formed during bending or tension when the yield strength is exceeded.

In general, the fish eyes are of microscopic size or the crack propagates along the primary austenite grain boundaries. Hydrogen accumulated in cavities may produce a pressure of about 100 MPa. In ordinary rolled steel, the inclusions are flattened, providing a high pressure area and sharp internal notches. Thus, exceptionally, the hydrogen pressure is sufficient to produce cracks in the rolling plane (blistering) without any external load.

The question arises, in what manner does hydrogen enter the matrix from the cavity (or also from the environment) during cracking. Certainly, this can only occur when hydrogen exists in its atomic state, *i.e.* hydrogen must be dissociated. This should be possible by adsorption on fresh surfaces created during deformation (Hofmann and Rauls [16]).

Hydrogen cracks can propagate rather fast. The transport of hydrogen before the crack tip can therefore not be realized by diffusion as this is a very slow process. Instead, some kind of hydrogen pumping has to occur. Such hydrogen pumping has been observed by several authors, 50 years ago, Bardenheuer and Ploum [17] found that steel wires charged with hydrogen lost a great deal of it during torsion or bending. Zapffe [18] compressed hydrogenized samples of Armco iron immersed in oil and noticed an ejection of gas bubbles at the slip bands and Neumann bands. This experiment was repeated by Erdmann-Jesnitzer [19] under more well-defined conditions. Extensive hydrogen release occurred with the onset of yielding, at compression values of 1% - 3%. Thus hydrogen can be squeezed out of a metal like a sponge. Alternatively, a strong uptake of hydrogen (tritium) under plastic tension was shown radiographically for austenitic Cr-Ni steel by Louthan *et al.* [20]. As an apparent contradiction, Hieber and Erdmann-Jesnitzer [21] observed a strong hydrogen release, also under plastic tension. However, this could have been due to hydrogen which had previously been accumulated in cavities and had to be desorbed from there first. For characterizing the described phenomena as being mechanically activated, the term "Tribo(de)sorption", suggested in the field of tribochemistry [22], was chosen.

Plastic deformation of metals occurs with the generation and movement of dislocations. Bastien and Azou [23] first assumed hydrogen atoms to be transported by dislocations. The carrier capacity of dislocations is also discussed for carbon and nitrogen and gives rise to the question of whether there is an essential difference between static dislocations and moving dislocations. A moving dislocation is a minute region in which the energy of deformation is converted into heat. Thus it cannot be excluded that the core of such a dislocation has a high temperature, possibly far above the melting temperature [24]. It was Späth [25] who assumed that the melting temperature is exceeded in slip bands. Based on this assumption, Rössler [26] concluded that the uptake of hydrogen during plastic tension occurs by thermal dissociation. Because of dislocation

transport, slip bands are enriched by the tribosorbed atomic hydrogen shown also radiographically by Louthan *et al.* [20]. This explains why the cracks propagate along slip planes ($\{110\}$ planes) according to Kikuta *et al.* [27].

In order to inhibit gliding, hydrogen has again to form molecules. The sites of such a recombination are assumed to be submicroscopic voids (vacancies being the smallest voids) produced by the interaction between dislocations (Bastien and Azou [23]). Then, these pressure bubbles should act like solid precipitates (Fig. 4).

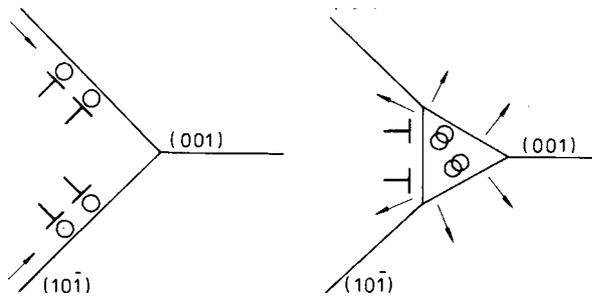


Fig. 4. Formation of pressure bubbles: voids are produced owing to the interaction of dislocations (Cottrell defect); the dislocations carry hydrogen atoms forming molecules in these voids.

4.2. Tribosorption of hydrogen under conditions similar to (blast) wear

In general, wear can be considered as a kind of fatigue fracture, see, for example, ref. 28. In both cases, loading occurs repeatedly and a large amount of deformation work is necessary to create and propagate cracks. The deformation is concentrated on the surface (in normal fatigue with a more distinct localization) and later near the crack tip. This enables hydrogen to be tribosorbed even from the water vapour in humid air with the result that the fatigue strength is markedly lower in normal air than in dry air or vacuum.

Using a mass spectrograph, Frank and Sweets [29] provided the first direct proof that, during wear, steel takes up hydrogen from the water vapour present in humid air. When a steel pipe was ground with sandpaper under a normal atmosphere, after a certain time, hydrogen was detected inside the pipe. Wetting the paper increased the hydrogen content by about two orders of magnitude. Frisch and Thiele [30] investigated the interaction of the atmospheric humidity with steel (steel balls) in a rotation mill. Thus hydrogen entered the steel during wear (tribosorption); at the same time, hydrogen also left the steel (tribodesorption). The latter phenomenon became evident when subsequent wear tests were performed in inert gas. Furthermore, only that portion of hydrogen which had accumulated in the outermost zone was driven out. Hydrogen from deeper regions needed more time (24 h) to diffuse to the wear zone.

In the aircraft industry, during grinding, steel has been found to take up such amounts of hydrogen from the cooling water that screws and threaded bolts broke after loading [31]. These parts had been made of high strength steel which is especially susceptible to hydrogen cracking. The formation of sparks during grinding proves that high temperatures are reached locally, enabling the thermal dissociation of water and the tribosorption of hydrogen to occur.

The facts described above support our assumption that hydrogen cracking is actually responsible for the medium-dependent mass loss in blast wear.

4.3. Experiments and results

The influence of media on blast wear has been extensively investigated on unalloyed steel St 38 at a stream velocity of 90 m s^{-1} and a stream angle of 90° .

The wear conditions and mass losses are presented in Fig. 5. The reference value was obtained by blasting only with dry sand (0). Blasting with sand and dilute sulphuric acid (1) or water (4) as media, raised the mass loss but, surprisingly, water had a greater effect than acid.

The mass loss further increased with the samples being charged electrolytically with hydrogen before blasting. The charging was performed in $1 \text{ N H}_2\text{SO}_4$ poisoned with $5 \text{ mg l}^{-1} \text{ As}_2\text{O}_3$ at a current density of 10 mA cm^{-2} for up to 20 h. As a result, there was no difference when blasting occurred with sulphuric acid (2) or water (5) as the suspension medium.

When the samples were charged with hydrogen during blasting by “cathodic overprotection” of -1850 mV (SCE) , the mass loss was still greater (6).

The highest uptakes of hydrogen and, consequently, the highest wear rates were achieved by charging the samples before as well as during blasting (3).

To suppress possible dissolution, the samples were “cathodically protected” at -1000 mV during blasting (medium, $0.1 \text{ N H}_2\text{SO}_4$). The mass loss was the same for both protected and unprotected samples.

A more restricted research programme was performed for stainless steel and St 38 at the lower stream velocity of 30 m s^{-1} , see also Fig. 5. The tendency remained the same: the mass loss increased with increasing hydrogen absorption. The inherent low hydrogen diffusivity of austenitic steel did not exert any inhibiting effect on the mass loss even if charging occurred before blasting. The reason may be that only the outermost zone is involved in wear and, furthermore, tribosorption is widely independent of the diffusion behavior of a substance.

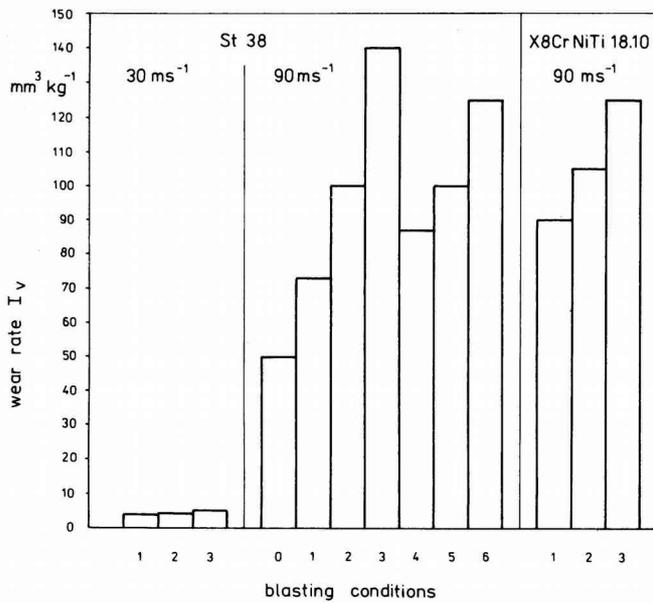


Fig. 5. Influence of pretreatments, media and polarization on blast wear of St 38 and X8 CrNiTi 18.10. Blasting conditions: 0, dry sand; 1, sand-0.1 N H₂SO₄; 2, samples charged with hydrogen, then blasted with sand-0.1 N H₂SO₄; 3, samples charged with hydrogen, then blasted with sand-0.1 N H₂SO₄ during further charging by overpolarization (-1850 mV, SCE); 4, sand-H₂O; 5, samples charged with hydrogen, then blasted with sand -H₂O; 6, overpolarization

At lower stream velocity, the influence of precharging is low for the unalloyed steel but, when charging occurred during blasting (including precharging); the increase in mass loss was high.

In the second part of the present work, the blast wear behaviour of the hardened steel C 60H was compared with that of copper and steel St 38 with the electrolyte, stream velocity and stream angle being modified.

The results are shown in Fig. 6, revealing some differences. For the hardened steel, the wear was higher in the acid than in water; the difference was even more pronounced at smaller stream velocities and smaller stream angles. For copper, the reverse is true: water slightly raised the wear rate which otherwise was reduced by dilute sulphuric acid to a value below that of air. Steel St 38, discussed previously in detail, showed an intermediate behaviour. The wear behaviour of the hardened steel C 60H, a relatively brittle material, was found to be similar to that of other brittle materials like cast iron, various ceramics and glass [1].

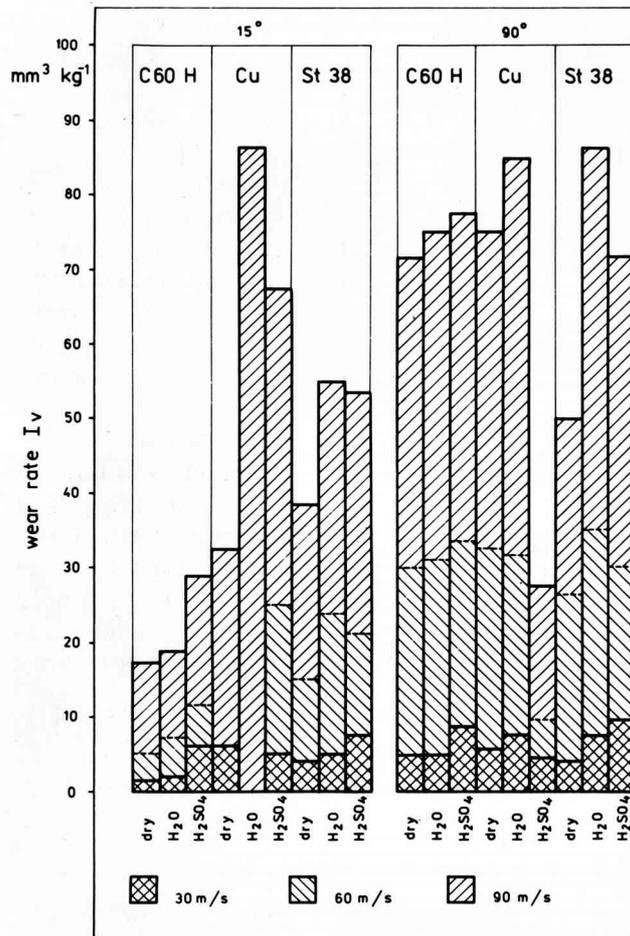


Fig. 6. Wear rate of steel C 60H, copper and steel St 38 as a function of electrolyte, velocity and angle of stream.

5. Discussion

Experiments have proved that wet media promote mass loss in blast wear. The assumption that this is due to corrosion (dissolution) does not hold true, which can be concluded from two findings.

(1) The corrosion current is too low; the measured values provide an explanation for a maximum mass loss of only 2%.

(2) Cathodic protection, which would suppress dissolution, is ineffective.

Moreover, hydrogen significantly increases the wear rate. This became clear when samples were charged with hydrogen before or during blasting.

The more hydrogen was introduced, the higher was the wear. This was particularly evident when charging the samples both before and during blasting.

The above findings allow the conclusion to be drawn that the wear activities of water and diluted acids are not due to corrosion but to hydrogen cracking. No ions but particles are produced. The hydrogen uptake for its part is the result of triboabsorption processes at the impact sites. The conversion of kinetic energy into deformation work (*i.e.* heat) should produce locally such high temperatures that hydrogen is thermally dissociated. The hydrogen atoms are swept into the lattice

by dislocations. In copper, (diluted) sulphuric acid reduces the wear rate below that of air which may be caused by strong work hardening and which was also observed. It is not clear how the acid can promote such work hardening.

The reference value used in the present work is the mass loss revealed by blasting under dry conditions, *i.e.* in air. However, the normal humidity of the air provides hydrogen. As mentioned above, fatigue strength is reduced by air humidity. Uetz [32] found out that, for severe gliding wear, the wear rate strongly increases with increasing air humidity. Thus the true reference value, excluding the influence of hydrogen, may be obtained only in dry air, dry inert gas or in vacuum.

We believe that our hypothesis is not only of academic interest. Two conclusions can be drawn concerning the countermeasures.

(1) The material should be more resistant to hydrogen cracking than to corrosion. This resistivity has to be tested under dynamic conditions.

(2) Inhibitors to prevent hydrogen uptake certainly differ from those to prevent corrosion.

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