STRESS CORROSION CRACKING IN HIGH STRENGTH STEEL—OR HYDROGEN EMBRITTLEMENT?

By I. Weibull

Head of Materials Lab., Saab Aircraft Co., Sweden

Abstract—Amongst the problems encountered in the use of high strength steels, that of delayed failure is one of the most complex. Some observations made at Saab Aircraft Company point to corrosion under stress as one possible source of such failures. In this paper, some corrosion tests under stress in a humidity cabinet with steels of different compositions and hardness levels will be described and their results analysed in comparison with practical experience. Some experiments were carried out to investigate if the failures were due to true stress corrosion cracking or to hydrogen embrittlement, induced by corrosion.

Zusammenfassung—Unter den Erscheinungen, die man in der Anwendung hochfester Stähle begegnet, ist der spröde Dauerstandbruch einer der meist komplizierten. Beobachtungen bei Saab zeigen auf Korrosion unter Spannung als eine der möglichen Ursachen solcher Brüche. In diesem Aufsatz werden einige Korrosionsversuche in einem Klimaschrank mit Stählen verschiedener Zusammensetzung und Härte beschrieben. Die Ergebnisse werden erörtert und mit der praktischen Erfahrung verglichen. Einige Versuche wurden ausgeführt um zu untersuchen, ob die Brüche durch wahre Spannungsrisskorrosion verursacht wurden oder durch Wasserstoffsprödigkeit als eine Folge der Korrosion.

Avant-propos—Parmi les phénomènes rencontrés dans l'usage des aciers à haute résistance, la rupture retardée est un des plus compliqués. Observations faites aux laboratoires de la Saab indiquent la corrosion sous tension comme une des causes possibles de telles ruptures. L'auteur décrit quelques essais de corrosion dans une chambre d'étuve avec des aciers de composition et résistance differente. Les résulats sont discutés en comparison avec l'expérience dans la pratique. Quelques essais étaient réalisés afin de décider si les ruptures étaient produites par la corrosion fissurante sous tension proprement dite ou par la fragilisation par l'hydrogène comme suite à la corrosion.

INTRODUCTION

With the exception of spring and ball bearing steels, before 1945 steels were very seldom used for constructional purposes at strength levels above 200,000 psi. There were various reasons for this reluctance but one of the most important ones was certainly that the impact strength of steel was considered to be too low at such strength levels. It was also known that the notch sensitivity in fatigue increased markedly with the strength level.

Two factors have radically changed our approach to strength levels in steel above 200,000 psi: First, the ever-increasing demand for lower weight and higher strength in aircraft parts and second, the advent of other competing materials with a high strength to weight ratio, such as the high strength aluminum-zinc-magnesium alloys and the titanium alloys. In many of these the impact strength is quite low as is also the notch fatigue strength. However, with due regard to such circumstances, these materials function well enough.

Thus, a rapid development began, which would permit an increased strength in steel without endangering the safety of aircraft. Two lines of approach were tried:

One aimed at developing a steel which, after quenching, could be tempered without any sacrifice in strength at a temperature outside the low impact strength region characteristic of most steels. A typical product of this line of approach was the Hy-tuf-steel, introduced by Crucible Steel Co. of America in 1948. This steel is capable of a minimum tensile strength of 230,000 psi with a very good ductility. The nominal composition is:

	C	Mn	Si	Cr	Ni	Mo
%	0·15	1·3	1·5	0·3	1·8	0·4

Still higher strength can be obtained in steels of the same type with a higher carbon content, such as Super-Hy-tuf, Tricent and others.

Another line of approach was to improve the properties and treatment of existing steels. In this way it was found possible to use the SAE 4340 steel to a considerably higher strength level than anticipated before. This is now the dominating steel in the USA for high strength steel parts in aircraft.

SWEDISH EXPERIENCE OF HIGH STRENGTH STEELS

In Sweden, a steel similar to SAE 4340 with the Saab designation steel 1366 was used for a long time for similar applications and at a minimum strength level of 185,000 psi. The nominal composition of this steel is:

	C	Mn	Si	Cr	Ni	Mo
%	0·30	0·55	0·25	1·0	3·2	0·25

About ten years ago the first difficulties in the use of this steel were encountered. Cadmium-plated threaded bolts failed under sustained load in a brittle manner. Extensive investigations showed this to be caused by hydrogen diffused into the steel during the plating operation. Therefore, for this steel and other high strength steels, cadmium plating was replaced by acid zinc plating and for critical applications all plating was avoided as far as possible. The time and temperature for baking after the plating operation were also increased.

In this way the troubles caused by hydrogen imbrittlement in plating were practically eliminated.

FIG. 1. Fracture appearance of a failed bolt.

However, these precautions in plating did not eliminate all delayed brittle failures. In a few cases bolts failed without having been plated or otherwise deliberately exposed to hydrogen.

These failed bolts had a hardness of about 450 H_V, corresponding to a tensile strength of about 215,000 psi, and they were made of the above-mentioned chromium-nickel-molybdenum steel, Saab 1366.

Common to all these cases was a pronounced brittle appearance of at least the main part of the fracture surface. A typical case is illustrated by Fig. 1. A micrograph of a crack adjacent to the fracture is shown in Fig. 2.

A common feature was also that the material of the bolts exhibited good ductility and impact strength as far as these properties could be determined. Further, we could not reproduce such brittle failures in the laboratory by purely mechanical means, such as tensile and torsion tests.

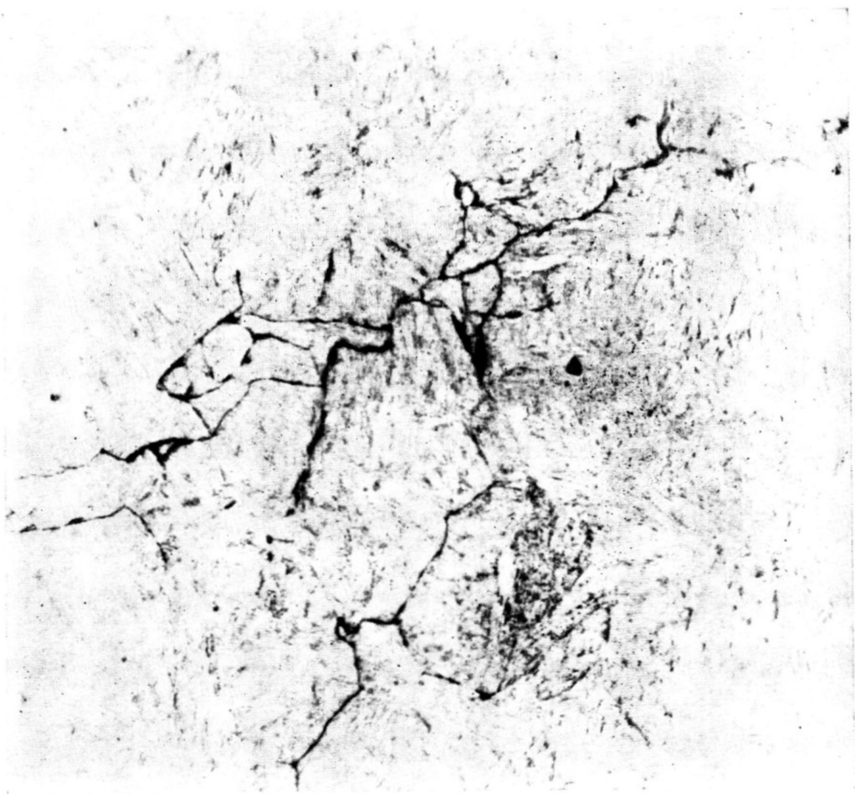

FIG. 2. Micrograph of crack in a failed bolt (Etchant Nital).

In one of those failures, corrosion played obviously a part. The bolt in question failed in the fillet between head and shank, and the failure started from a corroded spot.

It is known that hardened and tempered steels of this type are sensitive to stress corrosion cracking in hot alkaline solutions, existing e.g. in steam turbines. In this case the cracks mainly follow the prior austenite grain boundaries, in the same way as in the failure cases mentioned above (Fig. 2). Therefore these failures too might possibly be explained as cases of stress corrosion cracking, the corroding medium being condensed atmospheric moisture.

CORROSION TESTS UNDER STRESS IN A HUMIDITY CABINET

To investigate this, corrosion tests were carried out in a humidity cabinet holding air of 100% humidity and a temperature alternating between 25 and 43°C. The test pieces had the form of bolts put into holes in steel bars (Fig. 3) and tightened by nuts. The tightening torque gave a nominal stress in the core section of the threaded part of approximately 75% of the yield strength of the steel.

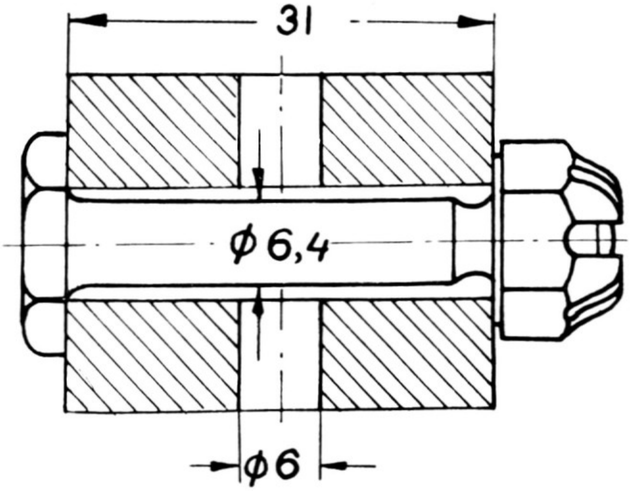

FIG. 3. Specimen and specimen holder for corrosion tests in a humidity cabinet.

These series of tests comprised steels of the four different nominal compositions given in Table 1. Steel Saab 1366 has been mentioned before (p. 336). Steel Saab 1546 is the Hy-tuf steel (p. 336). Steel 1624 is a weldable chromium-molibdenum steel for all-round aircraft purposes. It has a moderate hardenability and is not capable of quite the same strength as the other steels mentioned above. Finally, steel SIS 2536 is a general purpose chromium-nickel-molibdenum steel, standardized in Sweden for applications, where high strength is required in parts of large dimensions.

Table 1 also shows the hardness levels of the bolts of the different steels, the torque applied (approximately proportional to the hardness) and the life in days in the humidity cabinet.

Thus it was found that most bolts failed after a certain time, ranging from less than a day to months. A typical failure is illustrated by Figs. 4 and 5 and a micrograph of a crack is shown in Fig. 6. From these figures the brittle appearance of the failures is evident. In many of the bolts, the

TABLE 1

Results of corrosion tests in a humidity cabinet with steel bolts of different compositions and hardness levels

Group	Steel	Composition limits %						Number of bolts	Hardness H_V	Torque kpcm	Life days
		C	Si	Mn	Cr	Ni	Mo				
1	1366	0·28 0·35	0·15 0·40	0·40 0·70	0·90 1·2	3·0 3·5	0·20 0·30	20	350	250	75
2	,,							20	425	310	13–85
3	,,							20	480	350	1–19
4	1546 (Hy-tuf)	0·23 0·28	1·3 1·7	1·2 1·5	0·20 0·40	1·65 2·0	0·35 0·45	10	490	375	14–36
5	1624	0·23 0·28	0·15 0·35	0·50 0·80	0·90 1·2	— —	0·15 0·25	10	385	300	> 60
6	SIS 2536	0·28 0·35	0·15 0·40	0·40 0·70	1·1 1·4	4·0 4·5	— —	10	480	350	< 2
7	,,							10	480	300	1–3

cracks were also very many-branched. Comparing now these figures with the Figs. 1 and 2 the very similar character of the cracks will be immediately recognized. Therefore the conclusion seemed to be justified that the two phenomena were very closely related.

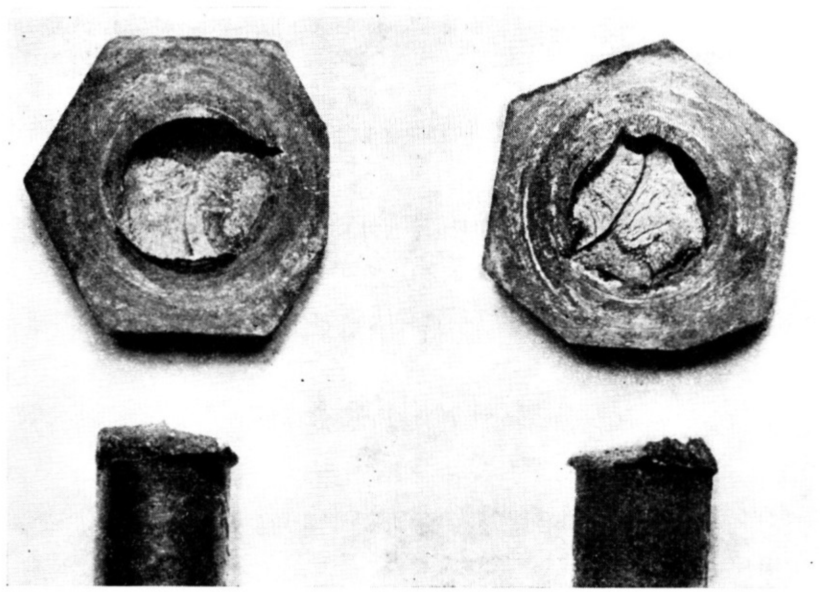

FIG. 4. Heads and shanks of bolts failed in a humidity cabinet.

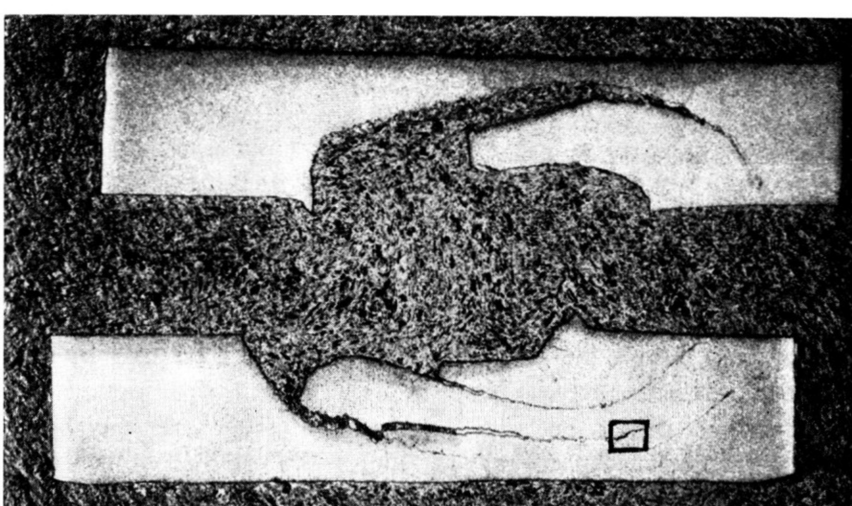

FIG. 5. Cracks in the heads of the two failed bolts in Fig. 4.

Turning now to the reaction of the different types of steel SIS 2536 had a very short life (Table 1, lines 6 and 7). In the second series of tests with this steel (Table 1, line 7) the torque and consequently the nominal stress was reduced by about 20%. The life of the bolts still was just a few days.

At the other end of the time scale there is the steel Saab 1624, which also had the lowest hardness. No bolt made of this steel failed within 60 days.

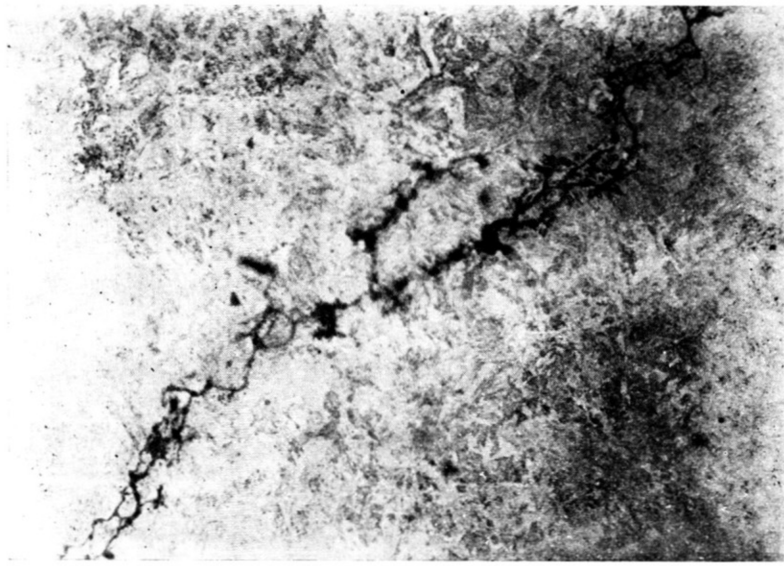

FIG. 6. Micrograph of the crack indicated in Fig. 5 (Etchant Nital).

The other two steels have an intermediate position. From the three series of tests with steel Saab 1366 (Table 1, lines 1–3) the strong influence of the hardness level is evident.

The Hy-tuf steel, quenched and tempered to a hardness level of about $H_v = 490$ gave a longer life than steel Saab 1366 of the same hardness level in spite of the slightly higher torque applied and was more comparable to steel Saab 1366 with $H_v = 425$. However, there may be some doubt as to whether these differences are statistically significant.

Experiments carried out with bolts stressed in the same way but in ordinary indoor atmosphere gave no failures during the period concerned nor were there any failures when no stress was applied. Thus it seemed to be conclusively proved that the failures were caused by a combined effect of the moisture and the stress.

CORROSION TESTS WITH WET SPECIMENS

A further series of corrosion tests were carried out in a somewhat similar manner. Thirteen specimens according to Fig. 7 were loaded in tandem in a creep testing machine as shown in Fig. 8. Tap water was led to each

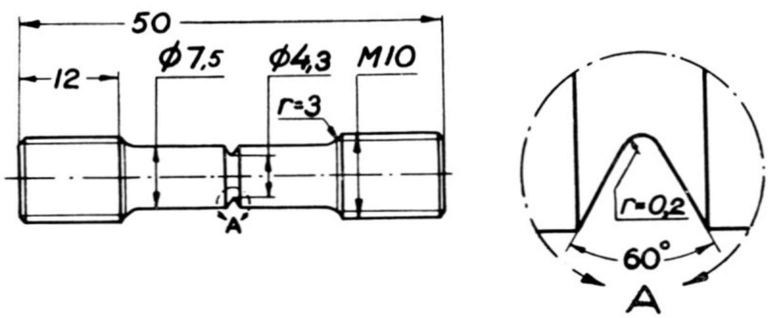

FIG. 7. Specimen used for creep machine corrosion tests.

one of 9 specimens by means of wick-yarn, one end of which dipped into a bottle filled with water. The other end was wound around the notch of the specimen. When a specimen failed it was replaced by a dummy (Fig. 8).

TABLE 2

Composition of steels corrosion tested in creep machines and in electrolytic cells

Designation	Composition in %							
	C	Si	Mn	P	S	Cr	Ni	Mo
Steel Saab 1546	0·25	1·2	1·4	0·015	0·005	0·24	1·83	0·42
Steel Saab 1624	0·23	0·31	0·64	0·017	0·008	1·10	0·12	0·20
Steel Saab 1626	0·32	0·28	0·65	0·016	0·014	0·93	—	0·21

Thirteen specimens were made of each of three steels the designations and heat compositions of which are recorded in Table 2. Steel Saab 1546 is the Hy-tuf steel referred to above, steels Saab 1624 and Saab 1626 are chromium-molibdenum steels with different carbon contents.

The specimens were all heat treated to approximately the same hardness level and the notch tensile strength of each steel was determined by means of specimens exactly similar to those shown in Fig. 8. In the creep

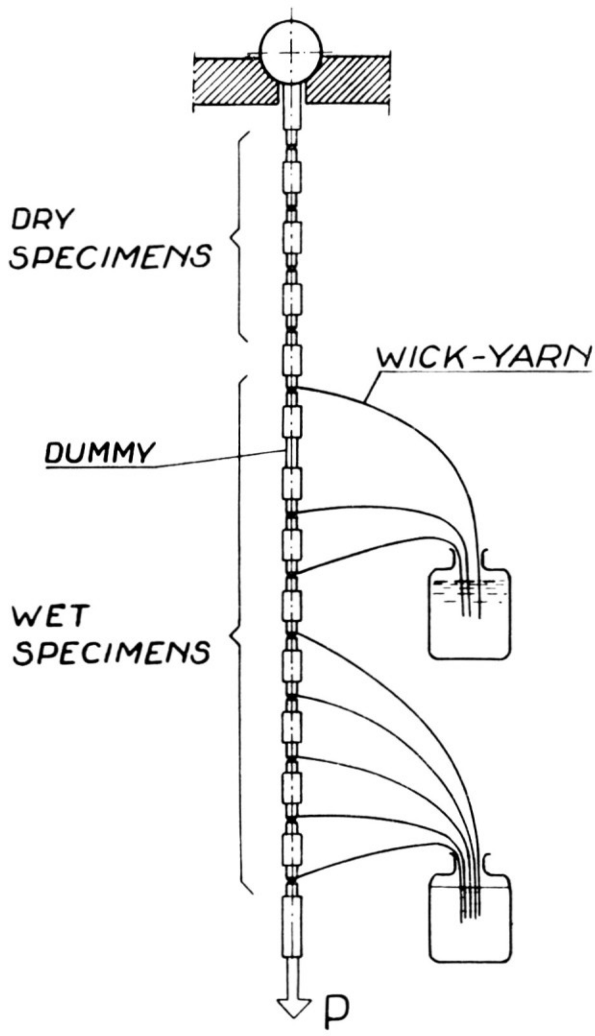

FIG. 8. Loading and wetting arrangement in creep machine corrosion tests.

machines, the chain of specimens was loaded to 75% of this notch tensile strength, which is given in Table 3.

In the same table the time to failure is recorded for all these specimens. It can be seen that the life of the specimens was very considerably reduced by the contact with water. It is also interesting to note the great difference between steel Saab 1626 and other two steels. Figure 9 shows a typical failure appearance.

One dry specimen of steel Saab 1624 failed after 170 hours, and after the conclusion of the test, small cracks were observed at the bottom of

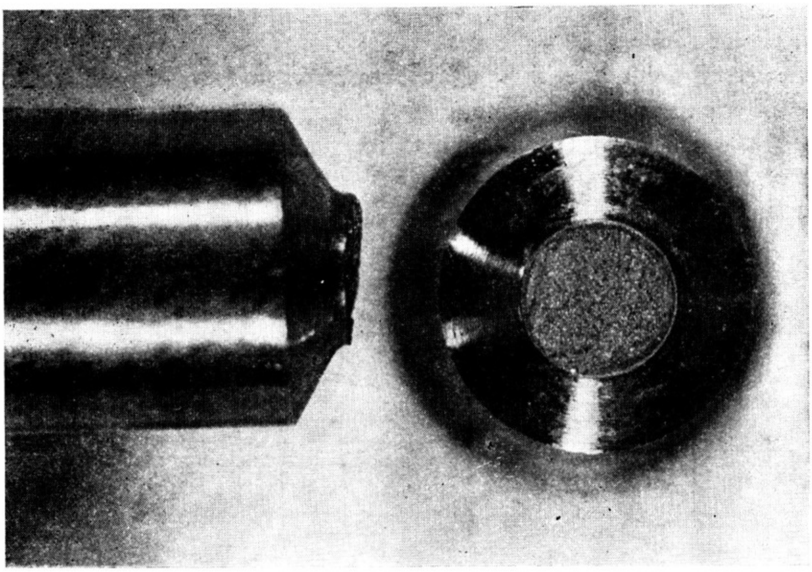

FIG. 9. Typical fracture appearance of specimen failed in a creep machine corrosion test.

the notch in all remaining dry specimens. Thus, the applied stress might have been a little too high. However, the influence of the water is still evident.

TABLE 3

Results of corrosion tests in creep machines

Steel	Notch tensile strength kp/mm²	Nominal stress kp/mm²	Life in hours of 9 wetted specimens		Life in hours of 4 nonwetted specimens	
			min	max	min	max
Saab 1546	276	207	100	132	> 300	—
Saab 1624	259	194	62	87	170*	—
Saab 1626	255	191	1·7	2·0	720	—

* One specimen of four failed, the other 3 were unbroken after 250 hours.

THE MECHANISM OF FAILURE

The results of the humidity cabinet tests do not necessarily mean that they were stress corrosion cracking phenomena in the true sense of this concept. It could also be possible that a small amount of hydrogen generated by the corrosion process had caused local brittleness and thus had started the failure.

From this point of view, it might be interesting to know if there is a similar difference in sensitivity to hydrogen embrittlement between different steels as there is in their reaction to the humidity cabinet test. For this purpose, modified tensile test specimens according to Fig. 10 *a* were prepared.

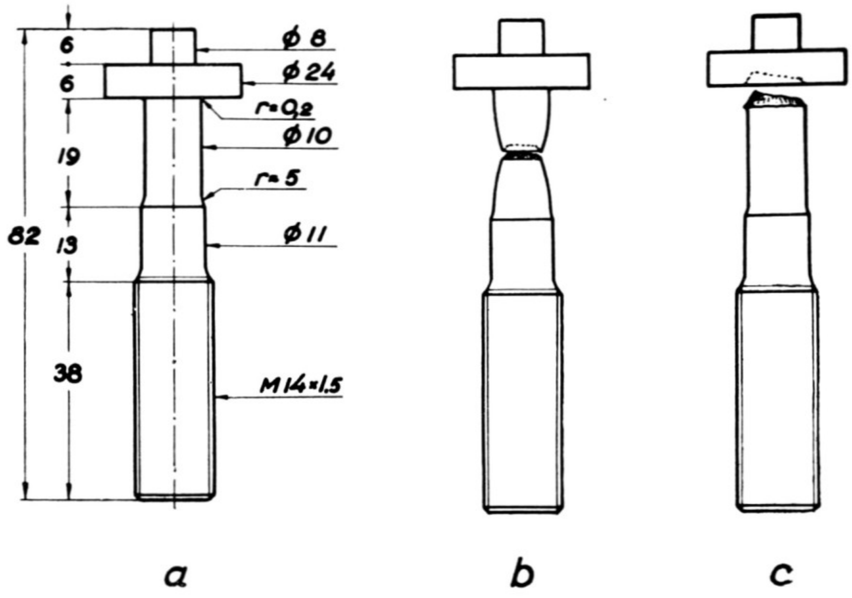

FIG. 10. Specimen for hydrogen embrittlement tests.

If tested without having been exposed to hydrogen, the specimens showed the normal reduction in area (Fig. 10 *b*). Embrittlement by hydrogen (e.g. in plating) led to the type of fracture illustrated by Fig. 10 *c*. In this case the fracture started in the notch below the "hat" and the nominal fracture strength dropped more or less as can be seen from Table 4. This table shows the reduction of the fracture strength (average of three specimens) after various plating operations known to introduce hydrogen into the material. The tensile strengths of the steels are also given in the same table.

Table 4 shows that the steel SIS 2536 is most sensitive to hydrogen embrittlement of the three steels tested and that steel Saab 1546 or Hy-tuf was not affected at all in this type of test. Thus the three steels rank in the same order as in the humidity cabinet test.

A failure showing some features in common with those mentioned above, was reported by Shank *et al.*[1] Some rocket chambers failed during hydrostatic water pressure tests. The extensive investigation carried out

TABLE 4

Results of hydrogen embrittlement tests with modified tensile test specimens (Fig. 11)

	Steel		
	Saab 1366	Saab 1546 (Hy-tuf)	SIS 2536
Tensile strength, kp/m^2	180	168	188
Reduction in % by:			
No plating	0	0	0
Cadmium plating, no baking	35	0	50
Cadmium plating, baking 17 h at 170°C	0	0	5
Acid zinc plating, no baking	20	0	20

to find the cause of these failures revealed a number of facts pointing to hydrogen embrittlement. It was assumed that the hydrogen had been generated by local corrosion, though the mechanism of hydrogen charging was not fully understood.

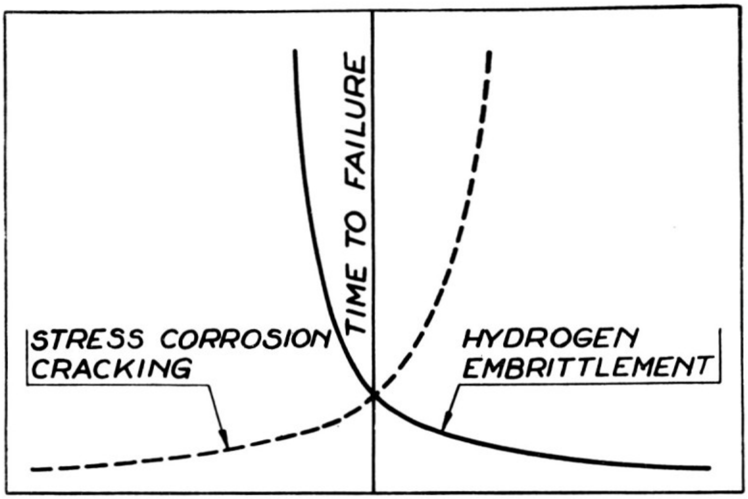

FIG. 11. Effect of impressed current on time to failure under constant load.

This is probably because in steel corrosion in neutral water solutions the dominating cathodic reaction is oxygen reduction[2], that is the reaction

$$O_2+4e+2H_2O = 4OH^-$$

and not hydrogen evolution

$$2H^++2e = H_2$$

Therefore it seems that the assumption of hydrogen embrittlement as a failure cause in these cases needs further support.

This support may be given by experiments according to a method used by B. F. Brown at the Naval Research Laboratory, Washington and others[3,4]. The material to be investigated is made one electrode in an electrolytic cell, containing the corroding solution concerned. With the test material under stress, a current is brought to flow through the cell. If, with the test material as cathode, the time to failure decreases continuously with increasing current, the failure is ascribed to hydrogen embrittlement. On the other hand the failures are stress corrosion cracking phenomena, if the time to failure decreases with increasing current and with the test material as anode. This may be further illustrated by Fig. 11.

ELECTROLYTIC CELL EXPERIMENTS

Preliminary experiments according to the method mentioned above were carried out in an apparatus shown in Fig. 12.

The specimen (1), which is shown in more detail in Fig. 13 *a* and *b*, was stressed by means of a steel ring (2). The stress was adjusted by means of the nut (3) and determined by a strain gauge (4) on the specimen holder. The corroding solution, which was distilled water, was brought into a small cell of plexiglass (5), put around the specimen. An outer E.M.F. was applied between the specimen and a ring of platinum wire (6). The current flowing through the cell was held constant until failure occurred or until the experiment was finished.

The first series of tests comprised five anodic, four cathodic and one neutral specimen of steel Saab 1546 (Table 2) of the shape shown in Fig. 13 a. Surprisingly enough, the specimens failed in a completely irregular manner and it was impossible to decide if the failures occurred sooner on the anodic than on the cathodic side. As could be expected, the rate of general corrosion was far greater on the anodic specimens than on the cathodic ones and outside the notch on the cathodic specimens the attack decreased markedly with increasing current. However, a close examination revealed that the character of the attack in the notch was the same in both cases. From this observation it was concluded that, owing to the poor conductivity and throwing power of the electrolyte (distilled water) the notch area did not react in a truly cathodic manner. This fact probably explained the lack of difference in time to failure between the anodic and the cathodic specimens.

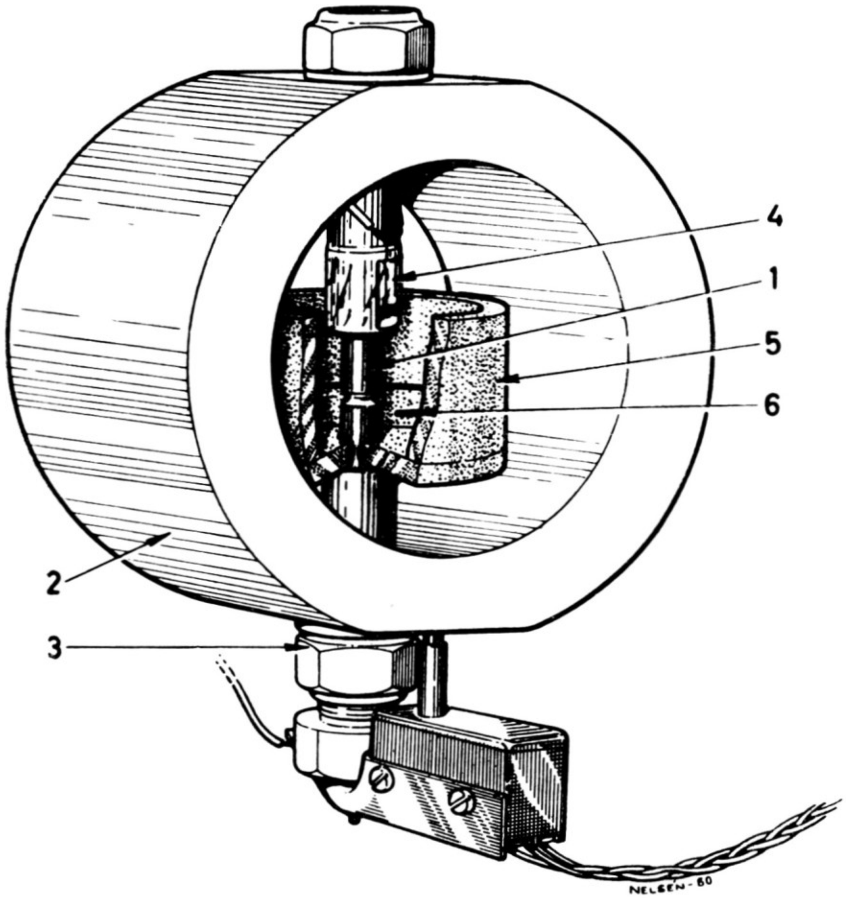

FIG. 12. Apparatus for electrolytic cell corrosion tests.

In weak electrolytes like distilled water, only small amounts of hydrogen will be generated, thus prolonging the time to failure. The hydrogen atoms entering the steel are assumed to diffuse to the area of maximum stress[1][5], which is close to the bottom of the notch. The effect of this is, that the time to failure under sustaining load is very much shorter for a notched specimen than for an unnotched one.

For this reason it was decided still to use notched cathodic specimens but the notch was covered with a thin layer of wax.

As the stress corrosion phenomenon fundamentally is not affected by a non-uniform stress distribution, unnotched anodic specimens according to Fig. 13 b were used.

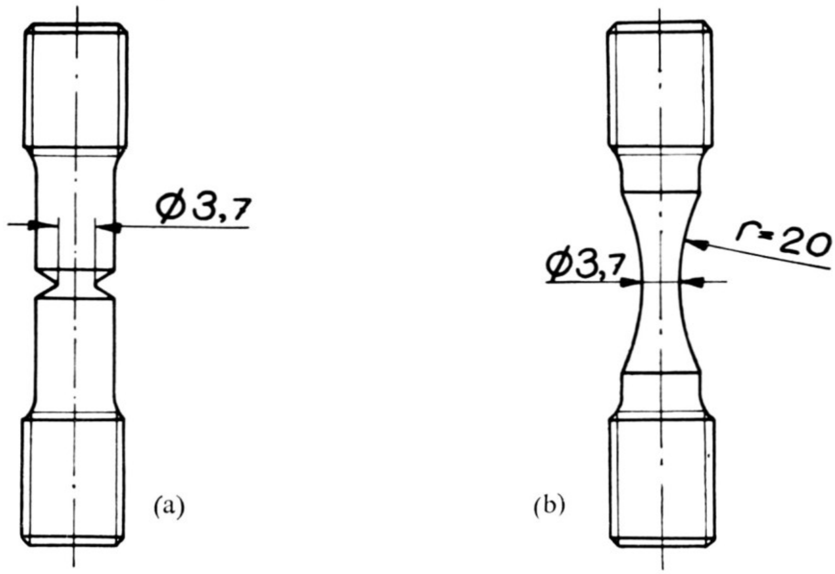

FIG. 13. Specimens for electrolytic cell corrosion tests.

Cathodic and anodic specimens were made of the three steels with the compositions given in Table 2. The cathodic specimens were stressed to 50% of their notch tensile strength and the anodic ones to 90% of their estimated 0·2% offset yield strength (Table 5). The current, being constant for each individual specimen, varied between 0 (open circuit) and $\pm 500\ \mu A$. The maximum current density thus was of the order of 100 $\mu A/cm^2$.

TABLE 5
Strength and stress figures for electrolytic cell specimens

Steel	Saab 1624	Saab 1626	Saab 1546
Notch tensile strength, kp/mm^2	266·5	245·6	284·7
Stress, cathodic specimens, kp/mm^2	133	123	142
Tensile strength, kp/mm^2	169·3	167·4	177·7
Estimated 0·2% offset yield strength, kp/mm^2	140	140	146
Stress, anodic specimens, kp/mm^2	126	126	131

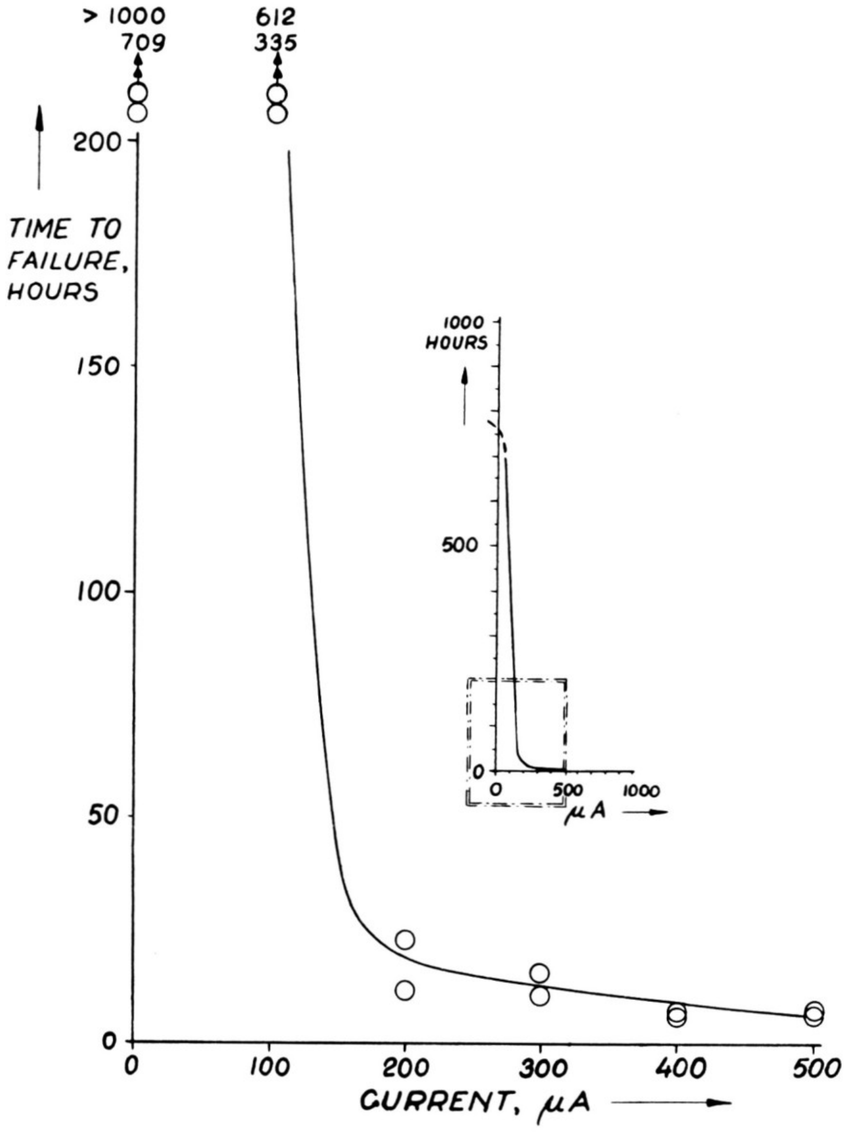

FIG. 14. Time to failure and impressed current for cathodic electrolytic cell specimens.

The pH of the water in the cells with cathodic specimens was about 6 at the start but during the tests decreased to 4·5–5, probably by absorption of CO_2 from the atmosphere.

The results for steel Saab 1626, the only one for which failures occurred within 50 days, are recorded in Table 6 and in Fig. 14. Figures 15 and 17 show the fracture appearances of one cathodic and one anodic failed specimen, respectively, while Figs. 16 and 18 represent corresponding micrographs.

The times to failure for individual cathodic specimens show a certain scatter (Fig. 14). However, the obvious trend is decreasing time to failure

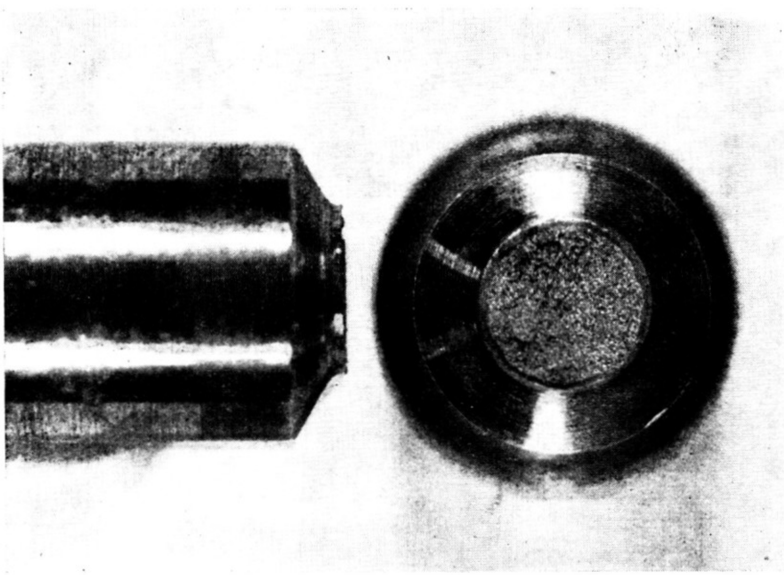

FIG. 15. Fracture appearance of a cathodic specimen failed in an electrolytic cell corrosion test.

with increasing current. According to Brown[3] this means that the failures were caused by hydrogen embrittlement, though the mechanism of hydrogen charging needs further study.

TABLE 6

Time to failure for electrolytic cell test specimens

Cathodic specimens Nominal stress 123 kp/mm²		Anodic specimens Nominal stress 126 kp/mm²	
Current μA	Time to failure in hours	Current μA	Time to failure in hours
0	709, > 1000	0	> 1000
100	335, 612	100	558
200	11, 23	200	546
300	11, 15	300	1000
400	6, 7	400	380*
500	6, 7	500	1000

* Test finished after 380 hours for examination of specimen.

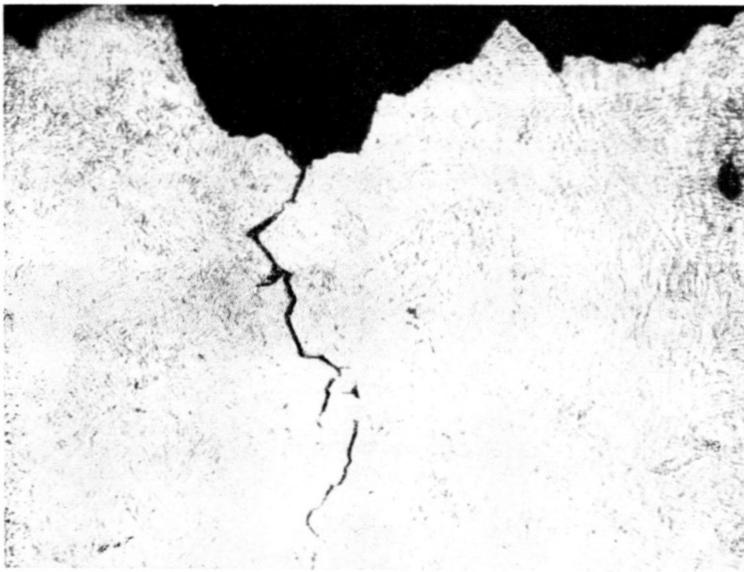

FIG. 16. Micrograph of crack adjacent to the fracture surface of the specimen in Fig. 15 (Etchant Nital).

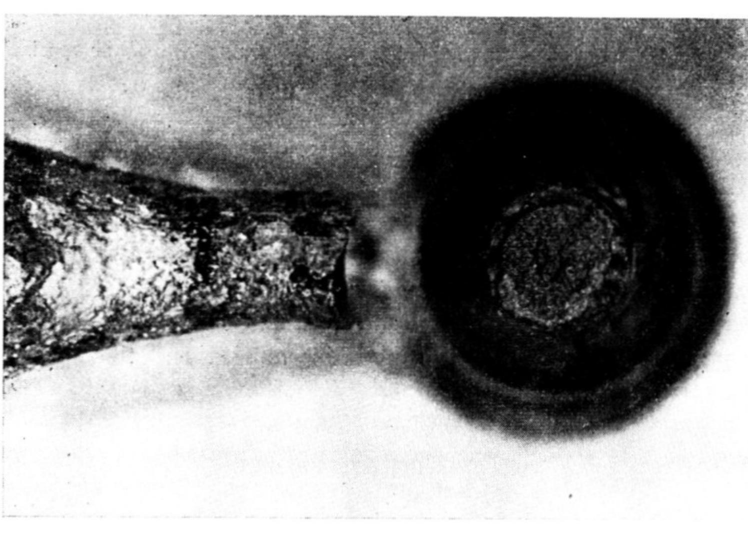

FIG. 17. Fracture appearance of anodic specimen failed in an electrolytic cell corrosion test.

The cathodic specimens were only slightly attacked by corrosion, the less the stronger the impressed current.

For the anodic specimens of steel Saab 1626 no corresponding relation can be traced, though two specimens failed within the time concerned (Table 6). These specimens were badly corroded (Fig. 17) and their stressed area was in this way reduced by about 10%. The corroded area showed

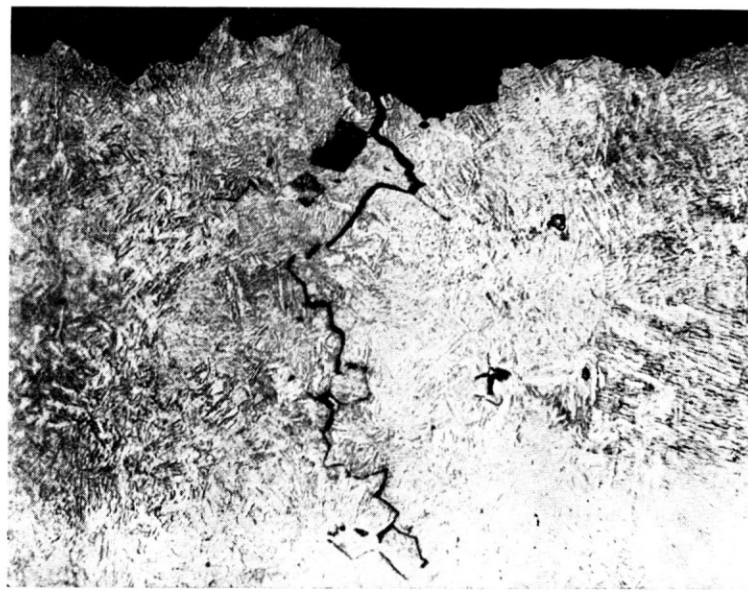

FIG. 18. Micrograph of crack adjacent to the fracture surface of the specimen in Fig. 17 (Etchant Nital).

no crack beside the main fracture (the small secondary crack shown in Fig. 18 was probably induced by the fracture). If these two failures had been true stress corrosion cracking phenomena, the specimens had very probably shown a number of cracks, as is the case e.g. when steel is attacked by an ammonium nitrate solution (Fig. 19).

Thus it might be concluded that the failures of the two anodic specimens were probably caused by their reduced area and the notch effect of the corrosion pittings.

THE PROTECTION PROBLEM

The protection against corrosion failures as those described above is not easy. Plating protects against corrosion, but there is always a cer-ain risk of hydrogen absorption from the plating solution. As the sensitivity to hydrogen embrittlement varies widely with the composition and the hardness of the steel, one plating method (e.g. acid zinc) may be fool-proof in one case but not in another. The only means of applying an acceptable metal plating without any chance of hydrogen absorption is

FIG. 19. Micrograph of cracks in a specimen exposed under stress to an ammonium nitrate solution (Etchant Nital).

vacuum deposition. But this method offers problems from a production point of view and the cleaning process may still involve hydrogen generating steps.

A good protection can be obtained by means of a well adhering grease, carefully applied. However, this poses certain overhaul problems, because such a protection must be renewed from time to time.

In this case it is also very important to fill pockets and narrow openings around the parts concerned with grease so that moisture cannot be retained there.

CONCLUSIONS

The following conclusions seem to be justified:

1. The brittle failures observed in non-plated threaded bolts of high strength steel were probably caused by hydrogen, generated by atmospheric moisture corrosion. The CO_2 content of the atmosphere may play a part in this connection.
2. The sensitivity to such failures and to hydrogen embrittlement in general is very different for steels of different compositions and hardness levels.
3. Protection against such failures is necessary but should not introduce a risk of hydrogen absorption during the protection process. From this point of view, application of grease or vacuum deposition of a metallic coating are to be preferred, but may pose practical problems.

REFERENCES

1. SHANK, M. E., SPAETH, C. E., COOKE, V. W. and COYNE, J. E., Solid–Fuel Rocket Chambers for Operation at 240,000 psi and Above, *Metal Progress*, November 1959, pp. 74–81, December 1959, pp. 84–92.
2. EVANS, U. R., *The Corrosion and Oxidation of Metals*, London 1960, pp. 88, 91, 309.
3. BROWN, B. F., *NRL Progress*, May 1959, pp. 40–42.
4. NAUMANN, F. K. and CARIUS, W., Bruchbildung an Stählen bei Einwirkung von Schwefelwasserstoff, *Archiv für das Eisenhüttenwesen*, April 1959, pp. 233–238, May 1959, pp. 283–292, June 1959, pp. 361–370.
5. MORLET, J. G., JOHNSON, H. H. and TROIANO, A. R., A New Concept of Hydrogen Embrittlement in Steel, WADC Technical Report 57–190, March 1957.