„Kinetics of Cracks caused by Hydrogen in Iron"

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Embrittlement, caused by corrosion, especially the formation of cracks at stress corrosion, has been estimated very often by the influence of hydrogen to crack formation.

These cracks will start (picture 1) ift local initial beginnings have caused a great probality for cracks of stress corrosion. This stress corrosion will damage the material very deep inside in course of time.

Crackformation as a function of time happens in steps. Picture 1 below shows these appearances of cracks.

This can not be taken as a rule, but this very often can be noticed at iron- and non-iron compositions.

Generally spoken there are nearly 2000 articles about this crack formations at iron-materials, the reports about welding technics included.

The problems with using the general kinetics of cracks at every special cases are, that the birth of cracks depends on the local distribution of hydrogen and its affinty caused by the distribution and also on the status of the hydrogen. The main influences are the strukture of the material (i.e. homogenious, or inhomogenious), the kind of phases, there properties according to the formations of fractures, there possibility to charge hydrogen and to be cold deformed (dislocation-kind, -density and -distribution). That means the history of the cold-plastic-deformation and/or the heat treatment has an influence of the behaviour caused by hydrogen.

Even the speed of lowering the temperature by normalizing in heat treating or recovery annealing has an influence.

Studies, made by the help of microscopes and electron microscopes, will show to the experts, that cracks which have been accured or will accure because of the influence of the mechanical stress, i.e. cracks caused by plastic flow of the materials, depend on very much varying conditions which may be present at that moment. If there have been cracks already, the fractures will depend on them, but if the cracks will begin at that time the field of stress has an important influence of the location of the crack caused by the geometry and kind of lattice.

The conditions of hydrogen in the iron - as an ion, atom or a molecule - has an influence. In opposite to that the source of the hydrogen is of a lower influence. That means on the other hand, that those investigations, which have not been made especeally for stress corrosion with hydrogen and its influence of the formation of cracks can be useful to find reasons for cracks in the structure, if there is no direct connection to the corrosive medium outside. That means, there is more knowledge about the influence of hydrogen as there is known from experiments about stress corrosion and the hydrogen influence.

It shall be reported about results of stress corrosion which have been found out by experiments. They were made in order to find a hypothesis which can be accepted because of its high probality about the way the crack will take in its late status of stress corrosion. To have not to many complicated influences of the

inhomogenious structures and to have simple conditionens and measurements at the tests, it is good to use pure iron, or homogenious i.e. CrNi-austenitic materials.

Even with pure iron the small impurities in there quantities and kind, dissoloved or not, and the form and distribution of inclusions (i.e. slags, especially micro-slags, which often have been over-looked) are of great importance for cracks caused by hydrogen. Cracks with slags can be observed, and those with i.e. carbides, but the inhomogenious distributions near the slags are of a great importants.

It must be separated:
Cracks inside which have already been present caused by hydrogen, also have an influence of the cracks.

Cracks inside, caused by hydrogen, which begin by mechanical, especially plastic flow, or even by elastic deformations when hydrogen is present before that special break happens.

The cracks at Armco-iron of efficient purity caused by hydrogen are normally transcristalline and can be seen in ferrit as a brittle failure inside, picture 2.

After having been charged electrolytically the cracks can not very often be seen microscopical but by the help of an electronic microscop as cracks with the forms of lines or areas and have been made by impact fracture at low temperatures, i.e. at the temperature of liquid nitrogen, and observed at room temperature with the electronic microscope. They show now the caused embrittlement.
The chemical inhomogenity, i.e. segregations, or inclusions, which nearly can not be seen, because of the rolling process, are of great importance, very pure iron with small additional carbon amounts show crack at the grain-bounderies, (2 b).

Normally we have transcris cristalline failure. If there is additional nitrogen, the cracks will always go through the ferrit grain.

It is of interest to consider the plastic deformation by the formation of cracks by watching the kinetics of the crack-formation caused by hydrogen at stress corrosion.

Transkristalline cracks inside, which seem to be plain, show in there run the direction of the cristall-formation, picture 2. The own statistic results of the length and cristall-formation oriented of the cracks show:
According to picture 3 those cristall-planes of the ferrit will become cracks, which are normally the slip surfaces at room temperature by plastic deformation. That leads to relations between hydrogen and dislocations which often have been shown, also in our own experiments. French works give a very clear idea of this, especially by having used tritium and electronic microscopical autoradiography, picture 4. Black spots show us that there are inhomogenious hydrogen distributions. Hydrogen will be enriched at the slip-surfaces of the ferrit and especially at or in grain bounderies (that means large-angle grain bounderies).

The distribution makes it possible to let us known something about the induction between the dislocations and the hydrogen. Own electrolytically thined foils of iron show us by beeing examined with the electronic microscope the different stages of the formation of cracks caused by hydrogen. These foils first had no loadings of hydrogen and only the normal amount of dislocations caused by the fabrication (homogenious spread black spots), picture 5, then they were charged with hydrogen, picture 5 b, and the stages of the formation of cracks can be seen as follows.

According to picture 5 b (as an exsample for many results of the same kind) changings at the dislocation distribution of the ferrit caused by hydrogen can be seen. Hydrogen causes an inhomogenious distribution.

The elementary beginning of the formation of cracks seems to start at very small cavities. The segregation of molecular hydrogen happens, as it can be expected, at lattice parts of low density, which have a high potential energie. It is very difficult to make sure by experiments, when the molecular form of hydrogen begins.

The question, if hydrogen in areas of high dislocation density has an influence of the bondings of the iron-atoms, has been discussed but is unsolved until now. At special places of the recombination of the dislocation cracks can be found, always at places of high density of dislocations, and these cavities will come together and make the beginning of a crack. Many micro-cracks beneath and above will be found. All those little cracks, which have no connections at the beginning, come more and more together, it can be suggested that this inside separations are caused by hydrogen. In the further run cracks of wide areas, picture 2, can be seen, i.e. near surfaces of metal plates. If there are extremely high amounts of hydrogen in big cavities near the surface, the well known expansions, which look like the irreversible pickling blisters, can be seen. Elongation at break, cupping ductility values, deforming and impact energy become smaller, when these inside cracks are present.

It will not be sure at which state of the formation of cracks according to the general kinetics of cracks we can speak of initial cracks or crack nucleus.

The same can be said about the "KIc-Factor" for we have a by cracks damaged lattice wthin the volume. This is according to the deformation locally of a limited extension. Many micro cracks in the volume are also of importance. The initial cracks should in practice be looked at real cracks in the iron lattice in the original sence.

After the ideas of W.S. Gorski, already mentioned 1935, (which has not very much been noticed in Western Europe) which can be read

Later on the loading times have been changed as well, as can be seen at picture 8. The time is a constant parameter for each curve. The quicker the torsion is the finer the cracks are, picture 9.

Herewith the influence of the grain-size, it can be seen a variety of the experiment-parameters together with the amount of hydrogen. Grain bounderies have much more dislotations and are good places for the recombination of hydrogen with a trap-effect. They stop a quick and deep penetration. To be full of dislocation means the same for the stop of diffusion at this place inside, as cold-deformed (before being loaded) iron or carbon steel shows i.e. at foils, where hydrogen goes through. This has been shown in several own works. Especially that pickling blisters come as a consequence of the rebombination of hydrogen at samples of iron and carbon-iron which were electrolytically loaded from one side.

Pickling with plastic deformations near the surface i.e. by shot pinning or sandblast has been in use for quite different are as of technic methods, i.e. to avoid fish-eyes caused by hydrogen at enameled sheets completely. The dissociation of the water in the frit and therefore the ofter of hydrogen to the sheet at the annealing of the frit normally takes place below the recristallisation-temperature. That means, the free hydrogen can not get inside the sheets and cause a secundary damage. Therefore the amount of hydrogen accepted by the samples of tortered Armco-iron depended on the grain-sizes the reason is the quantity of dislocations. Picture 10 a until 10 c shows that again schematically.

In a case that really has nothing to do with corrosion, fish-eyes and blisters in welded material of unalloy steel, as picture 11 shows schematically, cracks caused by hydrogen can be seen at the appearance of fracture which, spoken in general, have the direction rectangular to the direction of trajectory motions. The direction of the fracture at the end is also rectangular to trajectories.

It could be shown that spots caused by hydrogen are very often the result of plastic deformations. They can be seen after having passed the yield point. The same things recently can be seen at α-Messing, and also in welded material, which means the same as in carbon-steels. The examination by γ-ray shows by watching the K_1 $_2$ lines at carbon steel, that the cracks have a brittle failures and are surrounded by ductile fractures. This formation of cracks depends of the deformation-speed. This can not be seen at impact-samples. F. Bischhoff and later own results have shown, that not only the quantity of cracks, but there size depends on the deformation speed until the fracture of the specimen.

The pores at the fish-eyes or cracks are the places of assembly. Very often a slag is inside the defect. The spot can be seen microscopically and shows a slag and the inside of the defect.

The defect happens, when a mechanical stress is higher than the yield point and plastic deformation begins.

What does that mean for the kinetics of cracks?

Hypothesis for work:

It can be expected that there is locally and timely front of cracks and defects before the damage of cohesion. This comes from the micro cracks especially from the hydrogen which has been accumulated at dislocations. This causes a local additional pressure which must be added to local tensiles. There have been doubts about this idea of an inside pressure from some people, but there seems to be a high probability for this idea because of the inner cracks. But obviously it never could really made clear when the inital cracks begin. The hydrogen will be taken away together with the dislocatio- This effect needs time, comparable to the thermal diffusion.

If this time will be given, as at stress-corrosion, the recombination in micro parts can take place and the cracks infront of this crack front begin. This flow has an influence of the crack formation so that it works in steps, because a further flow needs the deformation and dislocationmovements, the transport of hydrogen to the next microcrack-place, recombination, crackstart as well as crack combination.

It may be made clear by this idea that very often failures happen in steps, which can be seen at iron and nonironmetals.

Trajano made resistants-time measurements at electrolytically loaded Armco-iron under stress. Picture 11 shows this steps caused during formation of cracks.

At this time, without any corrosion, only caused by electrolytic hydrogen ~~during~~ stress which can be elastic or plastic may be present. The yield point can be reached, but also steps may accure below this point, and cracks will be present. But this kind of formation of cracks may be different.

Picture 12 shows the welding material at the root face, but this is a fine grained steel, and it shows the same steps of cracks caused by hydrogen as an own result made with measurement of sound energies and formation of cracks as a function of time by the help of very sensitive primary elements according to investigations by J. Beges and D. Rehfeldt. This structure partly is of martensite. The measurements of sound energies show wider steps than it can be caused by the grain size, that means, the steps are not cause by the grains.

After reports about the latest statues of formations of cracks at stress corrosion, and if a lot of other results about cracks caused by stress without any corrosiv agent, and cavities infront of the cracks together with the step, picture 1, it will be taken in

account that the here given hypothesis for work seems to be obvious; that means a timely damage of cohesion in steps infront of the formation of cracks caused by stress corrosion is the real reason for brittle failure. In this way transcristalline and intercristalline formations of cracks caused by hydrogen and dislocations are from the same kind.

If other gases, as chlorine i.e., can cause damages as hydrogen here, will not be discussed here.

It is of interest, that microscopical-time experiments of formations of cracks at stress corrosion of normal chrom-nickel steels, as found out by H. Grieße, degas by special deformations. But very often this degasing process comes to an end. Not every crack begin leads to a failure. Even just after tearing degasing can be watched by microscopes at the surface of the failure. It may be found out by further experiments which gas has been produced and comes out. To use gaschromatographic with argon as an innert gastransporter will be the right way to solve the problem.

It seems that there have been no equipments in use for the indication of such small amounts of gar.

Spoken in general the influence of hydrogen makers it difficult to use the criterious of the kinetic of cracks. It may be difficult to built in the rules of these kinetics of cracks in the general rules of the kinetics of cracks. The report of J. Beges, F. Erdmann-Jesnitzer and D. Rehfeldt at this composium will give a first quantitative relation, which combines the amount of hydrogen, the formation of cracks an a general K I c-Wert.

Picture 1 — Transcristalline and Intercristalline Formations of Cracks in Steps at Stress Corrosion and Zone of Plastic Deformation before Crack Begin, schematically

by E.N. Pugh, Nato Science Committee 1971, Ericeira/Portugal

Picture 2 a — Cracks parallel to the Surface of the Steel Sheets after having been Charged Electrolytically

by F. Erdmann-Jesnitzer and H. Hieber

Picture 2 b — Cracks Caused by Hydrogen at Large-Angle Grain Bounderies Wedges, Metallographic Findings, not etched

by F. Erdmann-Jesnitzer

Picture 2 c — as Picture 2 b; but an Electron Micrograph of the Fracture with Polycristalline Fracture-Habits of a Polygon and a schematically Coordination of 120° Angular Position, as well as Fine Grains

Picture 3 — Leadoff from an Electron Micrograph of Fracture-Studies, Crack-Length orientated by the Cristall in Ferrit with Hydrogen

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Picture 4 — Electron Micrograph and Radiographic Examination of Hydrogen Distributions (Tritium) in Polycristallin Iron

by Lapasset, Aucoutrie and Lacombe (1972)

Picture 5 a — Relativly Homogenious Distribution of Dislocations at Electrolytically thined Armco-Iron-Foils, not charged with Hydrogen, Electron Micrograph produced by Transmission Method

Picture 5 b — as 5 a, but Foils being Electrolytically Charged, Dislocation surromeded by Hydrogen, Beginning of transcristalline Formation of Cracks inside, right picture, compare picture 3 and the Crack Length

Picture 6 — Above: Apparatus for Compression of Electrolytically Charged Iron and Collecting of Hydrogen. Measurement of Hydrogen by Effusion by Volumeter, Samples have been Deformed plastically

Under: Curves of Compression-Tension and Deformation, Hydrogen by Effusion via Compression-Intensity

by F. Erdmann-Jesnitzer and H. Sabath

Picture 7 — Deformation by Torsion at Armco-Iron-Wires
Above: Apparatus for Electrolytically Chargings
(left) Bubbles of Hydrogen during Charging, no Plastic Deformation
(right) Charging with Hydrogen during Plastic Deformation

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Picture 9 — Fractured Surface of Charged High-Purity-Iron treated by Torsion and Embrittlement-Fracture
A: General View of Fractured Surface
B: V = 1 Revolution per Minute
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c) Electrolytically Charged with Hydrogen and Amounts of Current a Fine Grained Material and Coarse Cristalline Material

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after Troiano (1972)

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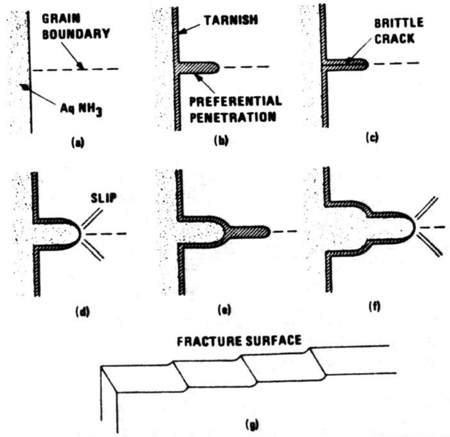
after J. Beges, F. Erdmann-Jesnitzer and D. Rehfeldt (1973)



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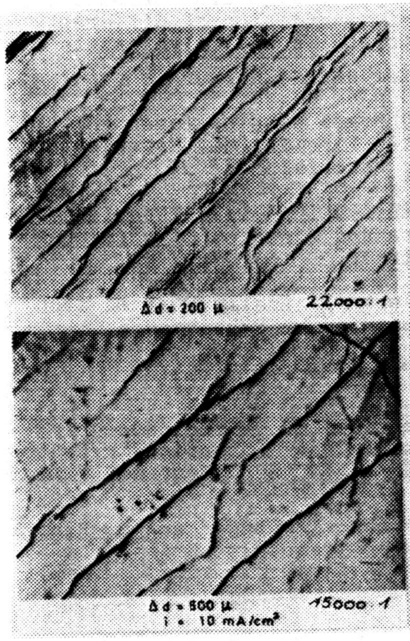

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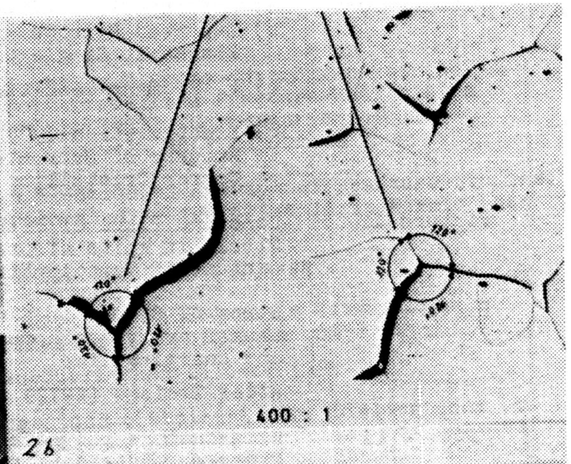

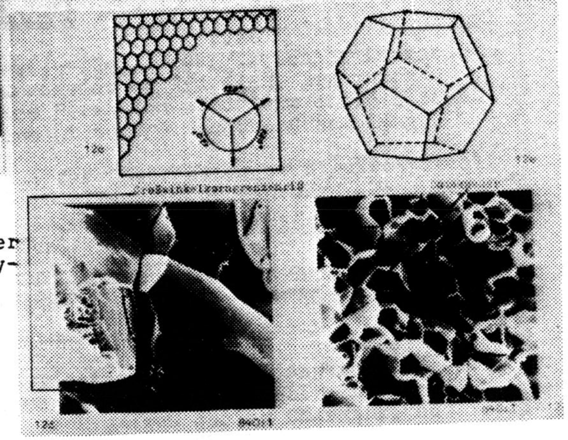

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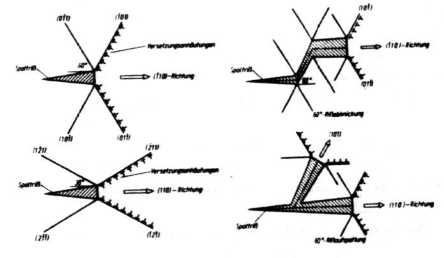

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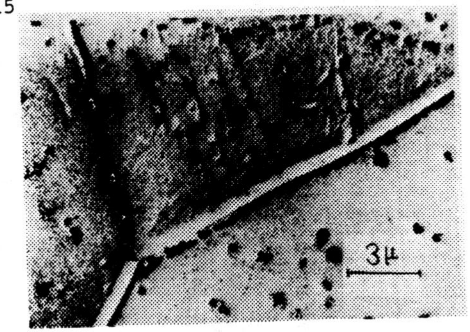

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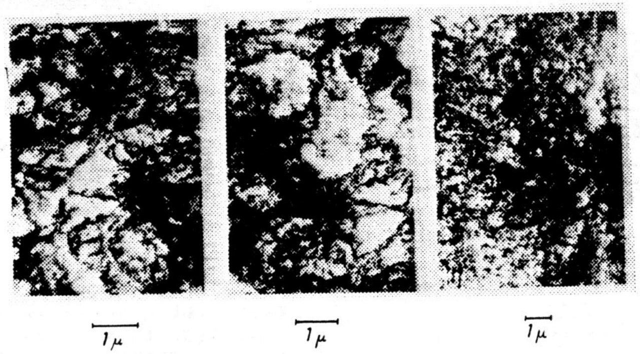

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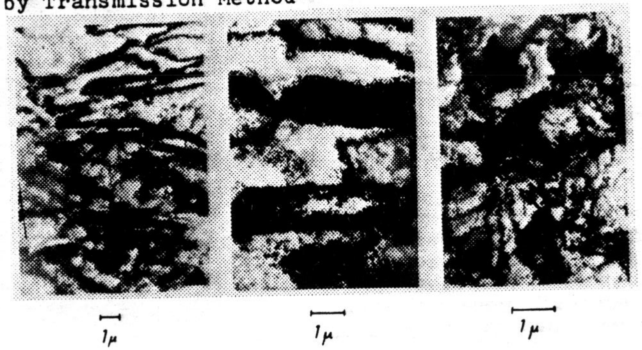

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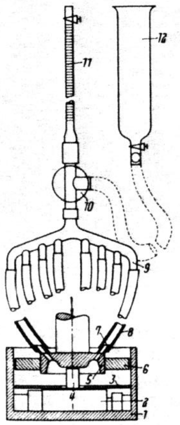

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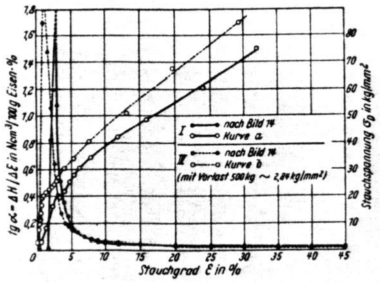

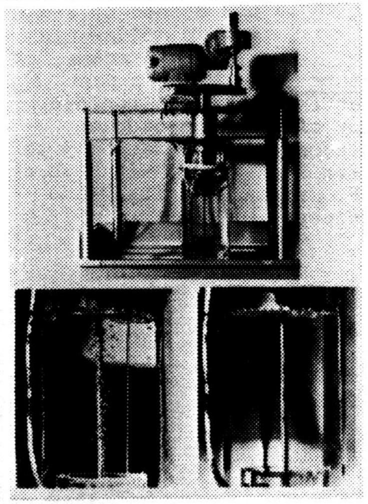

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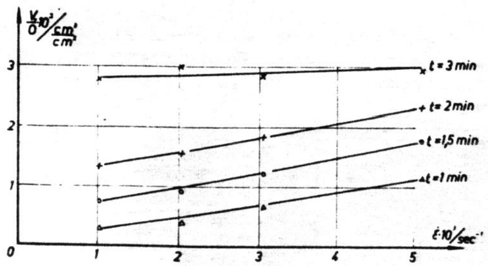

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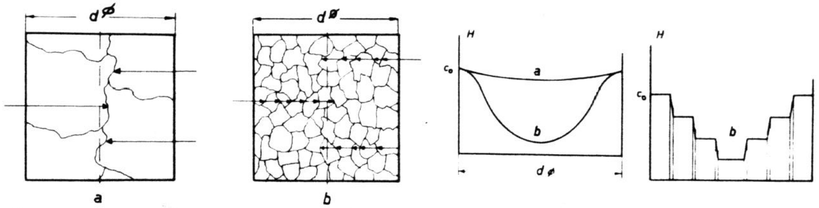

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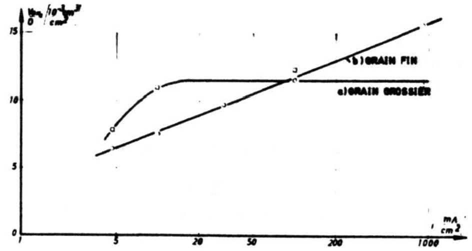

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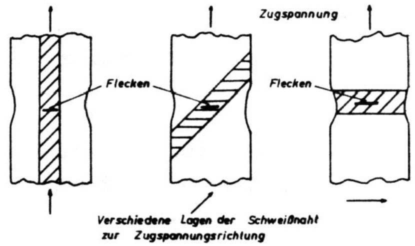

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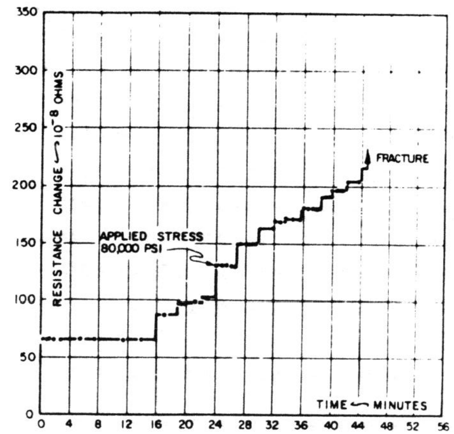

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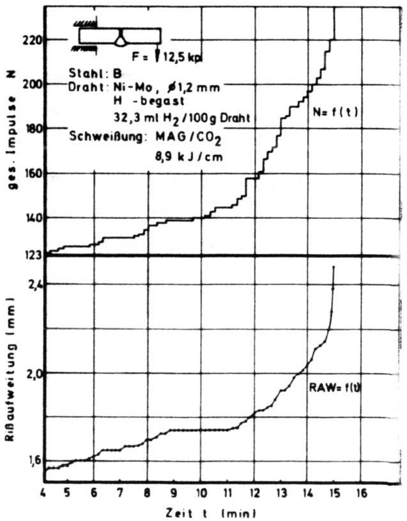

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