# NAVAL RESEARCH

## REVIEWS

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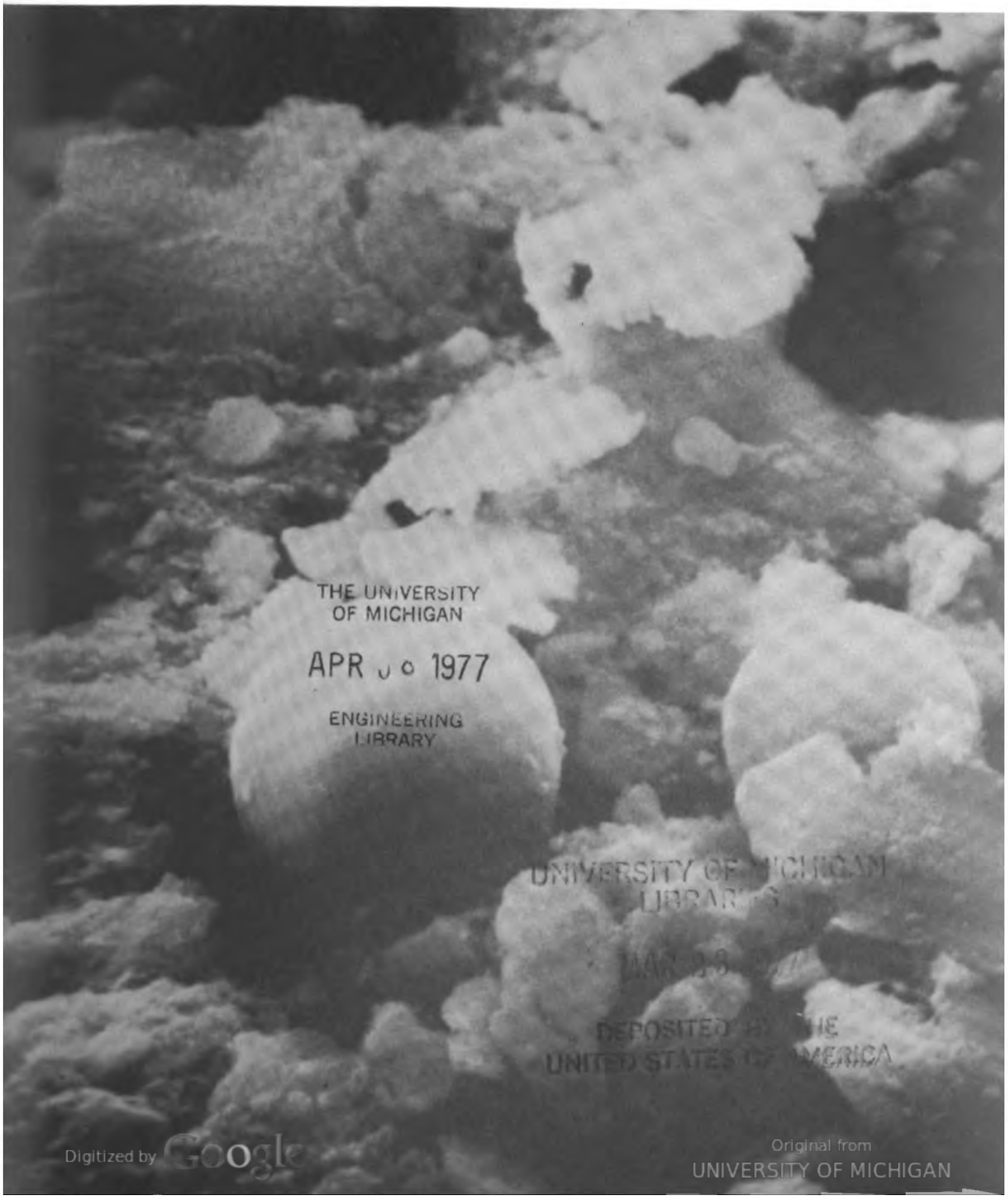

# PROFILES IN SCIENCE

*Dr. Ivan Sutherland*

Dr. Ivan Sutherland has been an ONR contractor for many years and for 7 years served as a member of the Naval Research Advisory Committee. His fame in the field of computer graphics began with a film entitled "Sketchpad", which he made from his thesis at M.I.T. in 1963. Next he became Director of Information Processing Techniques for the Advanced Research Projects Agency (ARPA), where he was influential in developing computer time sharing programs.

With David Evans in 1966, Sutherland founded in Salt Lake City the Evans and Sutherland Computer Corporation, which specializes in display systems for scientific uses. The company developed a remarkable 3-D picture-making technology which describes objects placed in a computer's memory in mathematical terms, and then converts them into color pictures.

Today Dr. Sutherland is Professor of Computer Sciences at the California Institute of Technology where he recently organized the computer sciences program. The focus of the program is the relationship and interrelationship between hardware and software through the medium of the design of integrated circuits.


*30th Anniversary Article*

# Ferrographic Analysis Recovering Wear Particles – from Machines to Humans

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## Introduction

When two surfaces touch and move with respect to one another the surfaces are changed. These changes result in wear and are, therefore, of great interest. With the development of the scanning electron microscope about twelve years ago the study of wear received a new impetus and it seemed for the first time that the complexities of friction and wear could be unraveled. All over the world scientists and engineers started to investigate these matters with a new intensity and persons of many disciplines found that they had contributions to make. The coining of the name tribology† a decade ago reflected this increasing interest, much as radio engineering became electronic engineering. The Office of Naval Research has been supporting tribology research for many years. Advances in this new science will lead to better designs and materials for ship machinery.

Earlier, during World War II, it came as a shock that the factors which determined the wear of electrical brushes were not understood. When the generator brushes in the first bombers and fighters to fly at high altitude wore out in a single flight no one knew what to do and the brush manufacturers seemed at a loss. Temporary solutions were found through trial and error but the first scientific explanations of the problem did not appear until 1946 or later. It was found that oxides of copper played a vital role in protecting the commutator surfaces. The lack of

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†From the Greek, tribos, or rubbing.

oxygen at the higher altitudes exposed the base copper, and the existing brushes wouldn't run on that material.

Questions like these have been studied for many years and by the time that tribology was recognized as a discipline and extensive wear literature existed. However, by no means was it possible to understand wear as a general subject. Factors that cause galling or gross incompatibility of rubbing surfaces were understood. An appreciation of the requirements of hydrodynamic and elasto-hydrodynamic lubrication was emerging. But what happens in a running machine posed many problems.

About five years ago, when the first Ferrograms were prepared, it was found that wear debris was not random "dirt" but instead that most metal wear particles belonged to a small number of types which are characteristic of the wear modes in the machine. The wear particles are usually drived from a sample of lubricating oil but they may also be recovered from the air or from the surface of worn parts. In any case, they are put in oil or water and analyzed.

It has been customary to disassemble a machine to determine how the parts are running. The disadvantage of this procedure, not to mention cost, is that one obtains only a snapshot view of what is happening. The worn surfaces show the last state they were in before the machine was disassembled. However, how they got that way remains obscure.

On the other hand wear particles can be obtained at any time by sampling the lubricant and so the "break in" and subsequent wear of the machine can be followed in detail. Since wear particles originate on a surface of the machine they contain a great deal of information about the surfaces and can reflect immediately the start of a severe wear mode. They are, therefore, very useful in studying the operation of a machine and in determining if the lubricated parts of a machine are running normally. In addition, wear particles are very useful in diagnosing specific faults.

To the extent that individual wear particles can be associated with their source, the state of individual surfaces can be determined. Not surprisingly, if the material of the particle is identified, many clues are available as to which part generated a wear particle. For example, it is a simple matter to distinguish wear of the cast iron piston rings and cylinders of a diesel engine from the wear of the valves and cams. The wrist pin bearings may give their signature by large bronze or other alloy particles. These, if found in numbers, would point to a part containing the alloy.

## Ferrograph

Before discussing the details of wear particles it is important to know what Ferrograms are and how they are made. The Ferrograph

analyzer consists of a pump that delivers the sample liquid at a low rate (on the order of 0.5 cubic centimeters per minute), a magnet that developes a high-gradient magnetic field near its poles, and a treated microscope slide. The magnetic particles adhere to a substrate on the slide, which is mounted at a slight angle to the horizontal. The oil sample is first diluted with a special solvent in order to increase the mobility of the wear particles in it. The diluted oil is pumped to the higher end of the slide and flows off the lower end, see Figure 1.

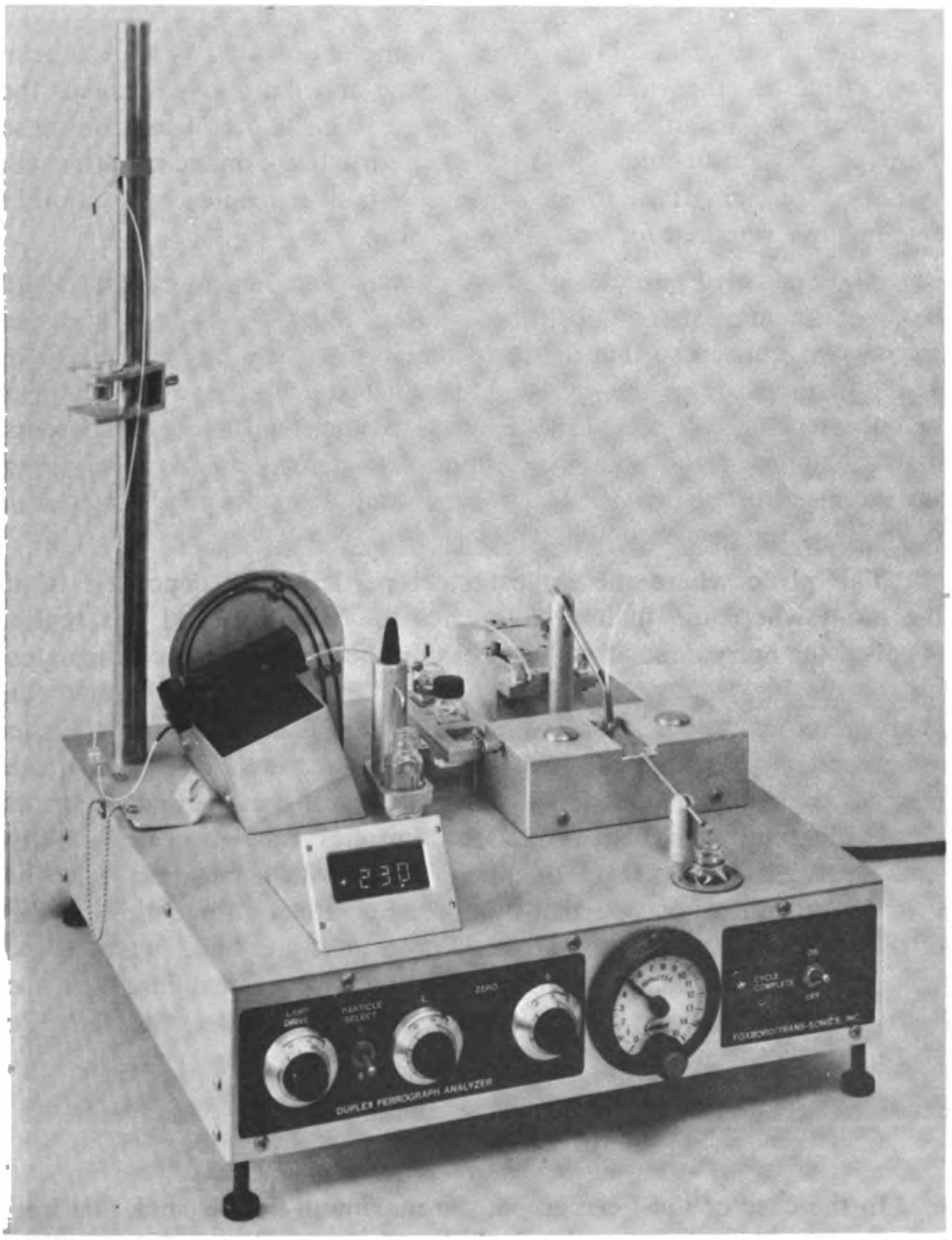


*Figure 1 — Duplex Ferrograph Analyzer*

The magnetic field is stronger at the exit end than at the entrance. As a result the particles are subjected to a continuously increasing magnetic field as they flow along the slide. In the presence of the strong magnetic field of the Ferrograph analyzer, all the steel particles, even the largest, are magnetically saturated so that the attractive force is proportional to the volume of the particle. The combination of the drag forces and magnetic forces causes large particles to be deposited first. Because of the higher surface-to-volume ratio of the smaller particles, they migrate through the oil slowly and flow with the oil for a greater distance before they are deposited.

After approximately two cubic centimeters of the sample has been pumped across the slide, a washing cycle and fixing cycle causes the wear particles to adhere to the substrate. The liquids used for these purposes evaporate quickly and leave the particles permanently attached. A normal pumping time for an oil sample is five minutes, with another five minutes required for washing and fixing.

The deposited particles ordinarily appear as a nearly invisible band along the center of the substrate. Figure 2 shows an unusually dense Ferrogram, chosen so that the deposit could be seen in the photograph. Large particles are on the right and the smallest on the left. Measurement of the attenuation of a beam of light passed through the deposit permits determination of the size distribution and density of particles along the Ferrogram (Figure 3). The readings are in terms of percent area covered by the particles.

The place where the largest steel particles are deposited is at the point where the fluid first touches the substrate and this region is called the entry deposit. Other areas on the Ferrogram are designated by the distance along the centerline from the exit end. As noted the Ferrograph analyzer employs a magnetic field to attract particles onto a substrate. The advantages of magnetic separation of particles are generally not understood and it is frequently suggested that electrical fields might be used instead. Indeed particles can be moved rapidly with electrical fields. However, precipitation with a magnetic field has the fundamental advantage that the force operates on the entire volume of the material. Electrostatic attraction, on the other hand, exerts force proportional to the charge on the particle, which may be different for the same particle depending upon circumstances. The shape of the particle also influences the electrical translational force.

## Wear Index

In the case of the Ferrograph, the maximum field is such that iron particles are close to saturation and, therefore, the shape of the particle

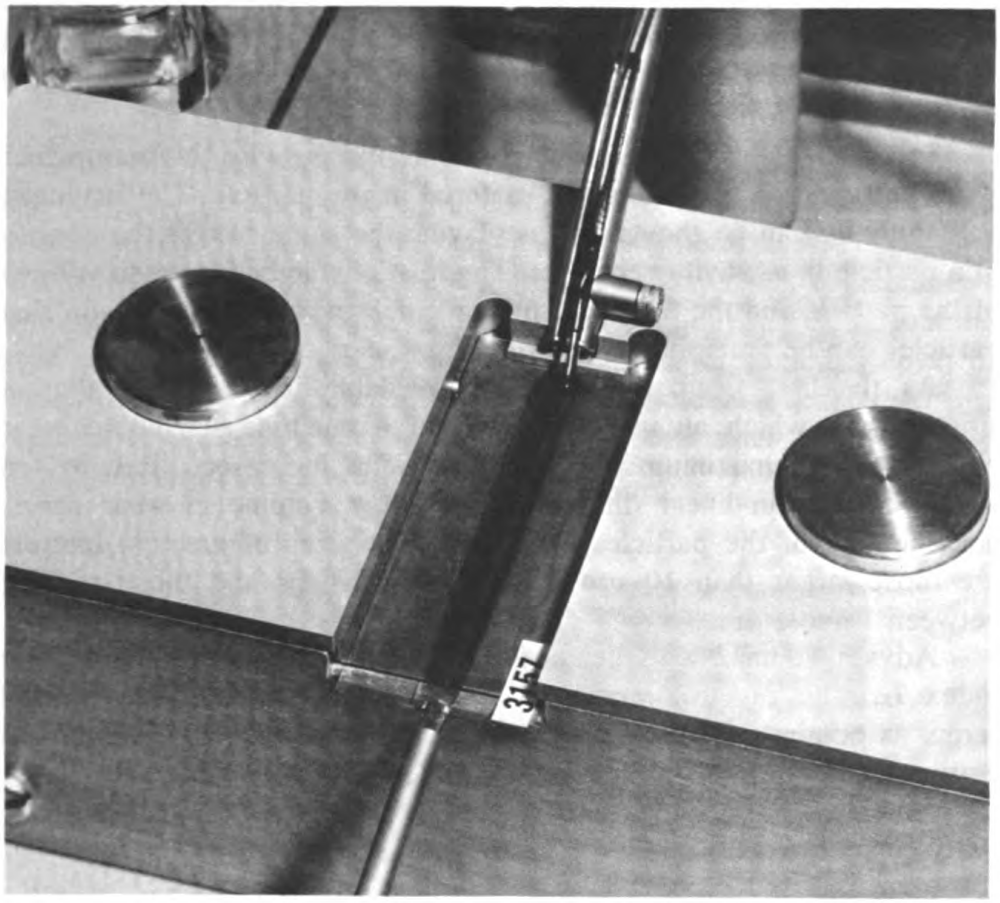

*Figure 2 – Wear particles being deposited on Ferrogram*

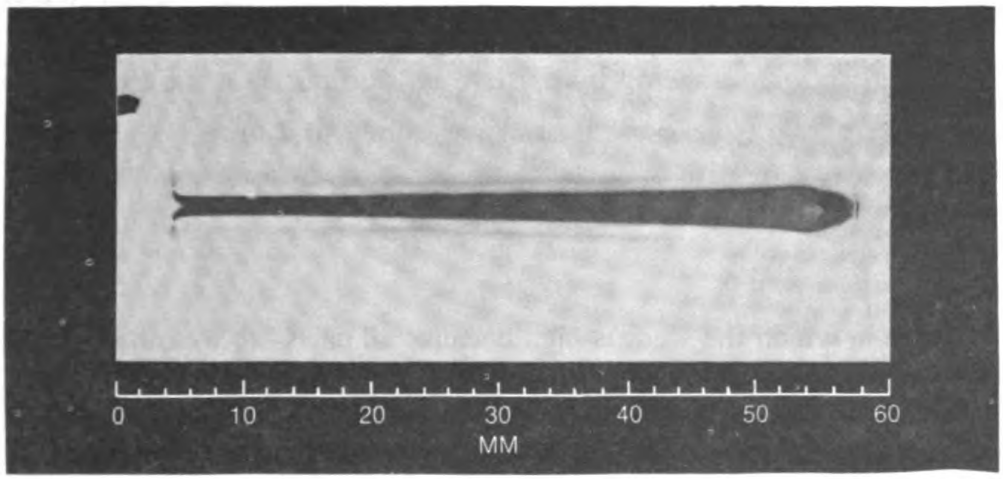


*Figure 3 – Ferrogram of deposited wear particles without oil.*

does not influence the degree of magnetization. On the other hand, paramagnetic particles have such a low coupling between their unpaired electron spins that the shape of the particle plays no significant part in determining its magnetic moment. Hence the volume of material determines the force.

In this respect the magnetic force is like gravity, a force which is proportional to the amount of material in the particle. The magnetic susceptibility can be thought of as playing the same role as the density of a particle in a gravity separator. The relationship between the volume of the particle and the force is a fundamental one and is the reason that particles can be precipitated according to size.

As the first Ferrograms became available it was noted that in situations in which an individual part of a machine started to wear excessively the maximum size of the particles increased, often by ten or more times in linear dimension. Both the volume of wear debris and the size of the particles increased. The sizes of greatest interest are those larger than 10 $\mu$m in major dimensions and those ranging between 1 and 2 $\mu$m.

Advantage has been taken of these facts to derive a severity of wear index $I_S$. The function expresses the severity of wear in numerical terms as obtained from a digital display that is part of the Ferrograph equipment.

$$I_S = (A_L + A_S)\,(A_L - A_S)$$

Where:

$I_S \equiv$ severity of wear index

$A_L \equiv$ percent area covered by particles at the entry deposit (steel particles $> 5$ um)

$A_S \equiv$ percent area covered by particles at 50 mm from the exit of the Ferrogram (steel particles ranging from 1 to 2 um)

The expression reduces algebraically to:

$$I_S = A_L^2 - A_S^2$$

In a case in which the wear is high because all parts are wearing rapidly the larger particles are missing and the factor $(A_L - A_S)$ remains low. Consequently $I_S$ remains low, even though $A_L$ and $A_S$ show marked increases. If a part enters a severe wear mode in which large pieces of the surface are removed, $A_L$ increases more rapidly than $A_S$, causing $I_S$ to increase.

A nearly equal increase in $A_L$ and $A_S$ indicates increasing general wear as may be caused by corrosive oil, sand in the lubricant, etc. If

both $A_L$ and $I_S$ increase, some part has entered a severe wear mode and the situation is consequently much more serious. When either happens the question is immediately posed, "What is wrong?"

## Rubbing Wear Particles

The tiny wear particles contain much information on that question. The particles are not random bits and pieces of the surface as it would be natural to think. Instead they belong to a few general classes depending on the mechanism by which they are produced. When a machine is running normally most of the wear particles are thin flakes called rubbing wear particles that range in size from about 15 micrometers down to a fraction of a micrometer. These flakes are seldom thicker than one micrometer and have a very short range crystalline order (approximately 30 nanometers). They are metals and not oxides. (Figure 4a and 4b).

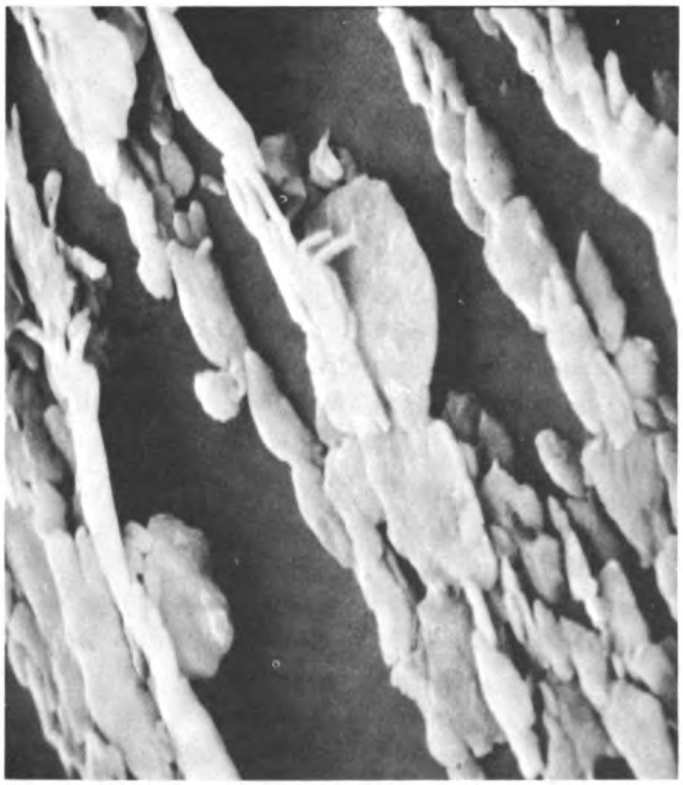

*Figure 4a — Rubbing wear particles as deposited on a Ferrogram. These flakes are generated in a sheer mixed layer on the surface of the metal. The layer is often about 1 μm thick and is thought to have very short range crystalline order, approximately 300 nanometers (300 x $10^{-9}$m). The flakes are generated in normal running of a machine and are almost always present. Such rubbing wear particles, when seen alone, indicate benign wear of a machine.*

*Figure 4b — Surface of wearing part. The smooth surface is composed of a sheer-mixed layer. Wear particles are in the process of breaking out.*

If the oil film on the surface is starved, the red oxide $\alpha$ $Fe_2O_3$ appears and is easily identified in the microscope. A further increase in the load under these conditions shifts the wear particles to the black oxide $Fe_3O_4$ with dissolved iron present. These distinctive particles have a black pebble like shape and are generated more often by hard than soft steels (Figure 5). Further increase in the load at the contact point results in shiny metal particles that range in size up to one millimeter and indicate total failure of the metal surface. By that time the machine makes bad noises, may smoke, and leaves no doubt that it is failing.

### Cutting Wear Particles

Among the more interesting categories are the cutting wear particles. They look like microscopic lathe chips and are caused by the interpenetration of one surface into another as might happen when an abrasive particle lodges in the soft material of a journal bearing. The presence of such particles in large numbers is abnormal and implies that a part of the machine is being destroyed by abrasive wear. If the cause is the presence of hard abrasives in the oil, the abrasive particles will also appear. It is a simple matter to identify silica, alumina, etc. (Figure 6).

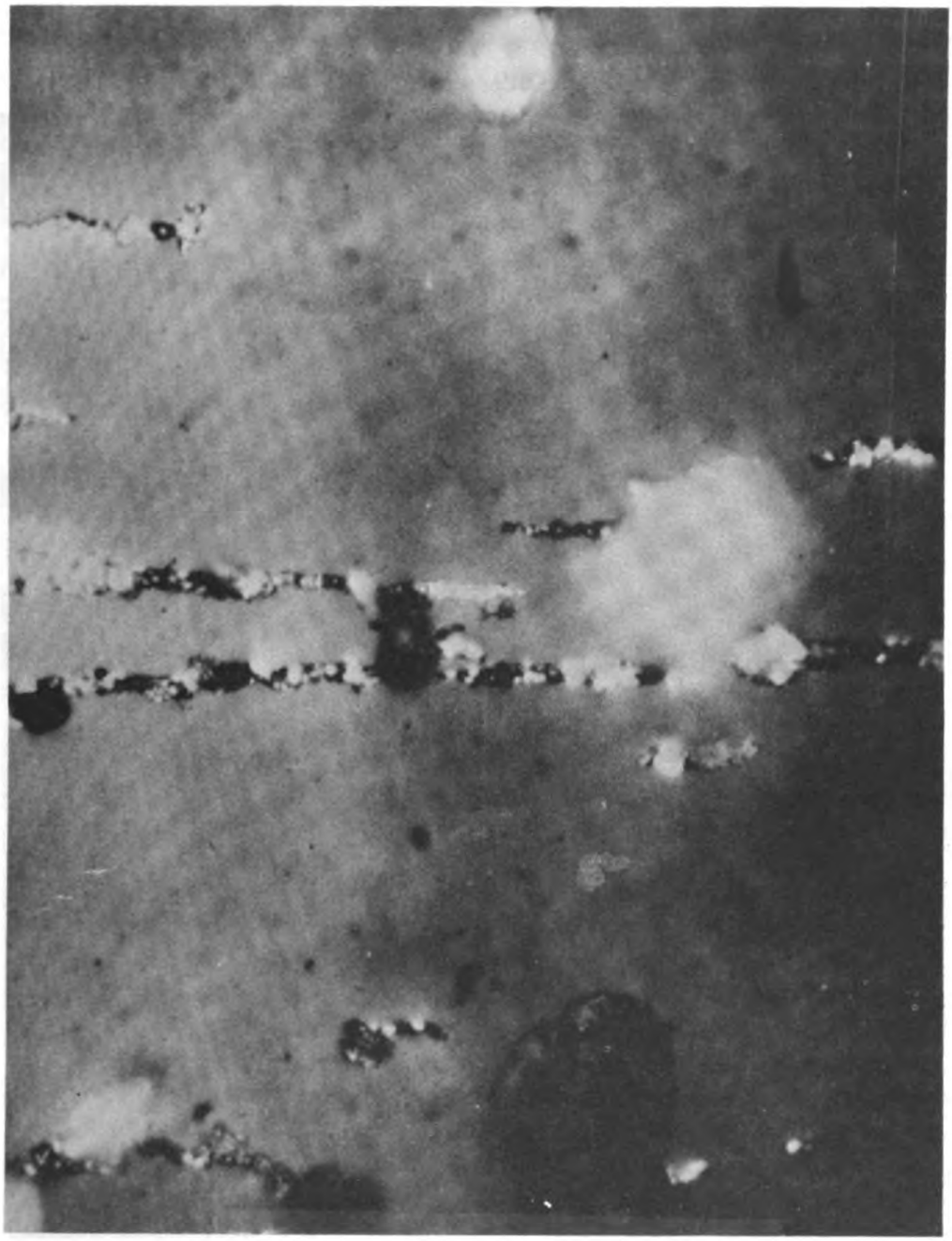

*Figure 5 — Strings of rubbing wear particles interposed with particles of the black oxide of iron, $Fe_3O_4$. Such black pebble like particles are usually generated with the harder steels, soft steels yielding before the necessary time and temperature are generated.*

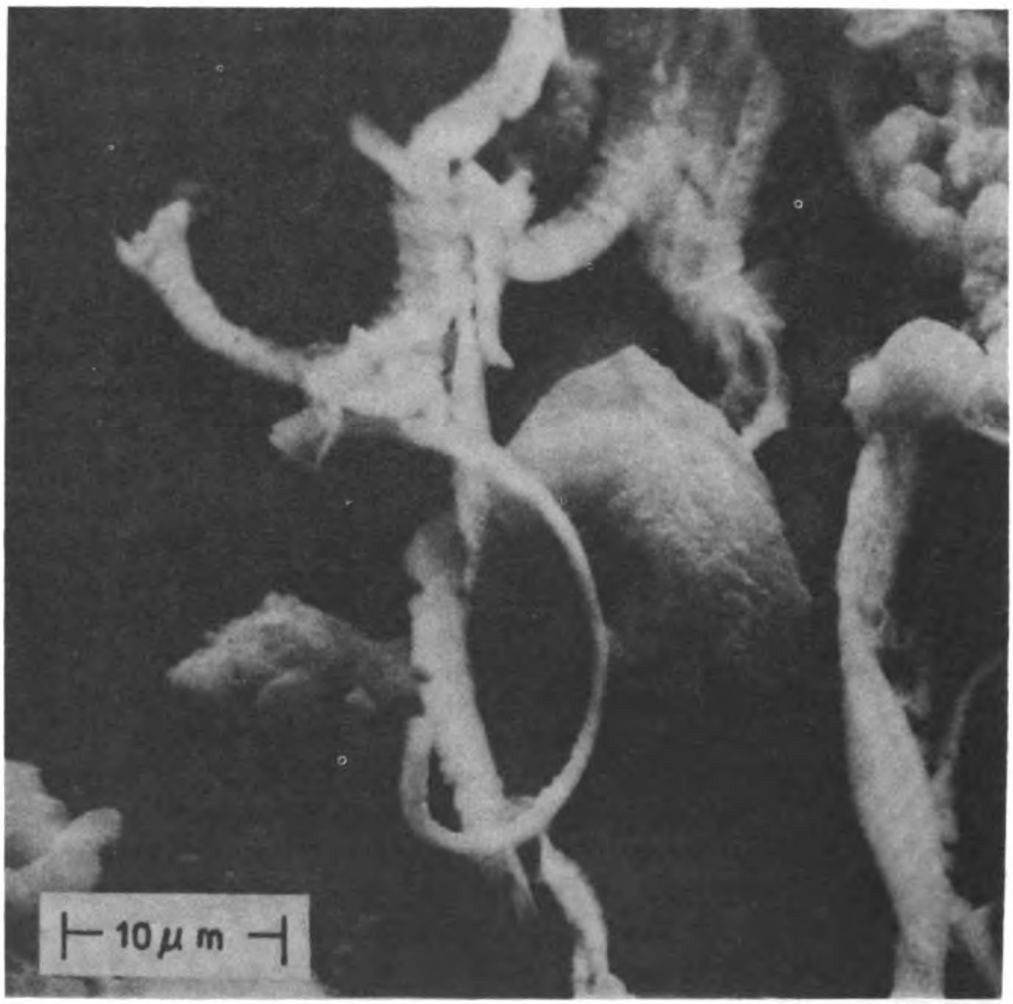


*Figure 6 – Cutting wear particles from a failing jet engine. When one surface interpenetrates a second, cutting wear particles are generated. Abrasive particles lodged in soft bearing collars often generate copious quantities of rubbing wear particles. In such a case the abrasive particles will also be present and may be identified as sand, aluminum oxide, etc.*

## Fatigue Chunks

Other particle classes include fatigue chunks and microscopic steel spheres which, when combined with laminar particles, indicate fatigue in ball bearings. A variety of polymers are sometimes generated from the oil by the catalytic action of the freshly exposed wearing surface. Different oils have their own characteristics when it comes to generating the polymers and tribologists are just now beginning to study these matters from an operational standpoint (Figure 7).

Much more could be told of the clues these particles provide concerning the wear status of a machine. However, I want to use the rest of this article to recount some very unexpected results in the precipitation of nonmagnetic materials. It is natural to think that Ferrography would be confined to investigation of magnetic materials, since the particles are recovered with a magnet, but it is not so.

## Non Magnetic Particles

From the start, nonferrous wear particles have been observed. They are magnetic as the result of rubbing against steel, as for example, a brass bushing against a steel shaft. They are easily distinguished from the steel particles because, being only weakly magnetic, they travel down

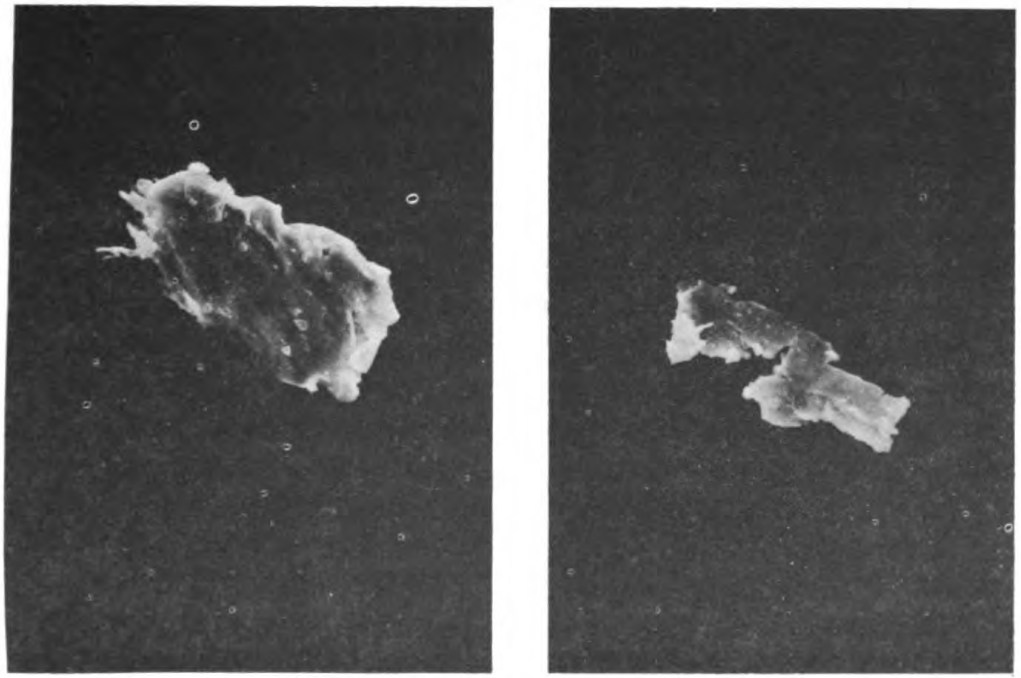

*Figure 7 — Fatigue particles are generated by the cracking of a surface. Cyclical stressing of the surface as might occur near the pitch line of a gear are necessar to generate such particles. They are relatively thick and are often more than 20 um across.*

the Ferrogram further than steel particles of the same size. They appear as large particles in a background of much smaller steel rubbing wear particles and often have distinctive colors such as the golden color of bronze. The plastics are deposited also but here it is a case of tiny steel particles being embedded in larger pieces of plastic. (Figure 8a, 8b, 8c).

Still many particles exist that are nonmagnetic and have not been rubbed against iron. What about recovering these? It occurred to us that if we couldn't attract the nonmagnetic particles perhaps we could make the liquid in which they were suspended magnetic. In that case the magnet would attract the liquid and repel the particles, a kind of buoyancy force. The force would be parallel with the field gradient as in the case of magnetic particles but act in the opposite direction. The first trials were inconclusive, some particles were repelled and some were attracted and both things happened with the same nonmagnetic materials! Were we kidding ourselves and dropping these particles

*Figure 8a – Two spherical particles on a dense Ferrogram. The spheres are steel. The serrated particles behind the larger sphere are small laminar particles. Larger laminar particles such as the one shown in Fig. 8c are easier to distinguish from rubbing wear particles. The combination of spheres and laminar particles occurs when fatigue causes micro cracks in a race or ball.*

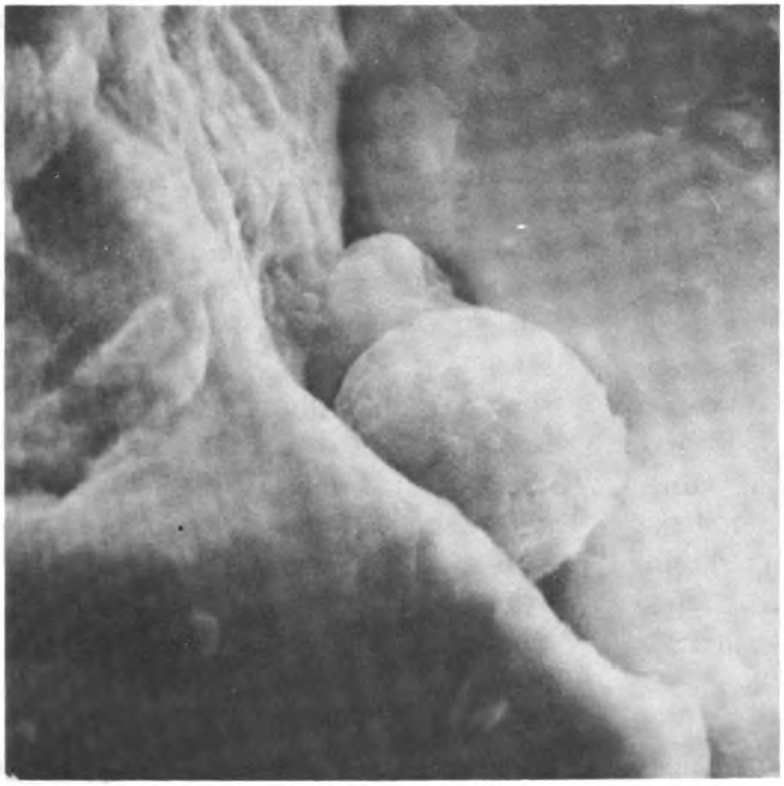

*Figure 8b — Steel sphere lying in a microcrack of a bearing ball. It is not unusual to find thirty or forty such spheres in a crack. Bearings have been observed to generate several million of the spheres in the course of fatiguing. Nevertheless the volume of metal in these tiny spheres is small compared to the volume of the cracks.*

*Figure 8c — A laminar particle. Such particles are often twenty or more micrometers across. Laminar particles are generated when a ball rolls over a metal piece. The resulting particles often has holes in its surface and serrated edges as the result of stretching the metal.*

by gravity? But then, with no magnetic field, almost nothing remained on the Ferrogram.

A happy accident pointed the way. One of the investigators (Westcott) was studying the precipitation of nonmagnetic particles at his home in Maine. Being far from the laboratory and wanting to get some particles to try with a new magnetic solution prepared at F/TI the day before, he reasoned that powdered sugar should be composed of small particles (it isn't). After raiding the kitchen, the resulting Ferrogram exhibited a clear separation. Nonmagnetic (diamagnetic) particles were found at the outer edge of the Ferrogram just where they were expected. These 4 $\mu$m diameter particles shone out brightly against a black background when viewed in polarized light at a magnification of 1000X. It wasn't long before it was realized that they were not sugar. They were starch put in the sugar to make it flow. These particles turned out to be an ideal tracer to show where nonmagnetic particles were being deposited. In a few days practical Ferrograms of nonmagnetic substances could be made.

## Human Joints

About this time Dr. Dana Mears, Director of Orthopedic Research at Children's Hospital, Pittsburgh, asked if wear particles from the synovial fluid of human being could be recovered. Synovial fluid is a viscid substance, somewhat like egg white, which lubricates the joints. It is a simple matter to suck out a few cc of the fluid through a needle. The synovial membrane makes more to replace the lost fluid. Would it be possible to precipitate human wear particles as the wear debris from machines is collected? (Figure 9).

The first patients analyzed had prosthetic hip joints and it was no surprise to find that particles of their tissues were magnetic since they had absorbed observable metal particles. The first Ferrograms of the synovial fluid, as well as those made from washings of the synovial membrane of a patient that had been operated upon, contained metal particles. Placing the Ferrogram in a scanning electron microscope made it possible to identify the metal particles as stainless steel from the surgeon's tools.* Their volume was low and they were not considered harmful but we recognized that the technique allowed us to trace such materials.

Synovial fluid from patients without a prosthesis does not contain magnetic particles and therefore we started to experiment with the magnetic fluids to see if we could precipitate particles of cartilage

*We wish to thank Dr. William Ruff of the National Bureau of Standards for analyzing the metals of these first Ferrograms of human tissues.

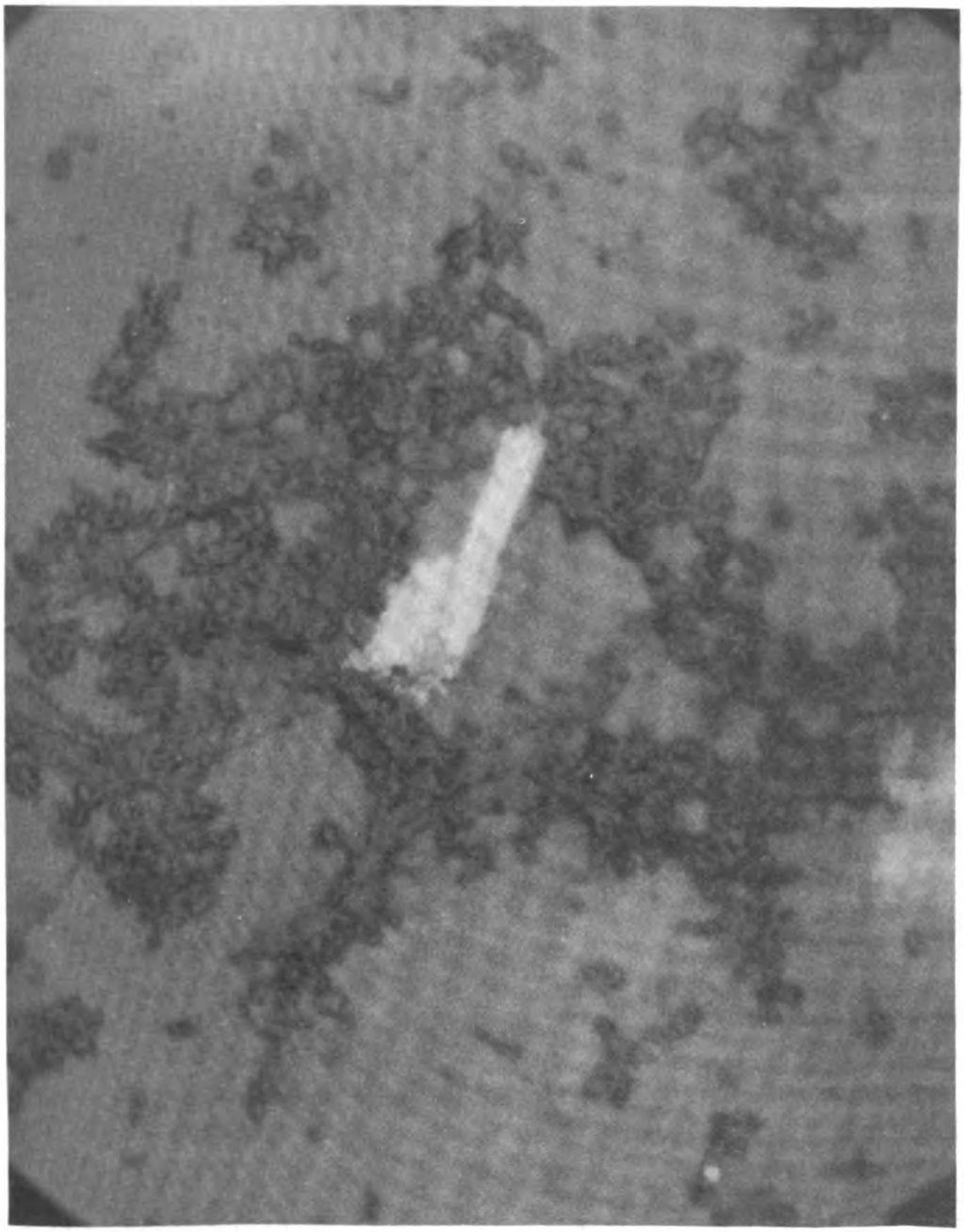

*Figure 9 — Ferrogram of synovial fluid from knee joint of patient having a torn meniscus. The gray deposit on the Ferrogram is tissue probably from the synovial membrane. The white particle contains cologin as for example cartilage. The photograph was made with reflected white light and transmitted polarized light with a crossed analyzer. Only optically active substances show transmitted light. This technique has been developed to reveal optically active materials, such as cartilage, in color, in the presence of other tissue. The optically active components appear red while nonactive tissue is green.*

and bone. Curiously, no particles followed our starch tracer to the outside of the Ferrogram. Instead a well defined band of magnetic particles and glycoproteins were seen along the center of the Ferrogram in the place where magnetic particles should be. The situation was more confused than is indicated here and we thought that we were in error.

However, after a few weeks we learned how to prepare fluids which caused these organic tissues to become magnetic. The action is one in which magnetic ions attach themselves to charge sites on the organic molecules. The game was chemistry. (Figure 10a, 10b, and 10c).

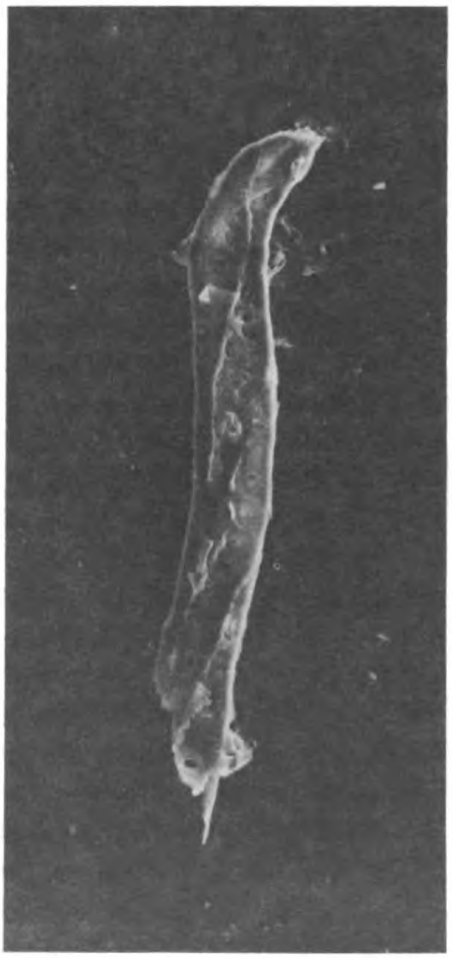

*Figure 10a — Particles of bone.*

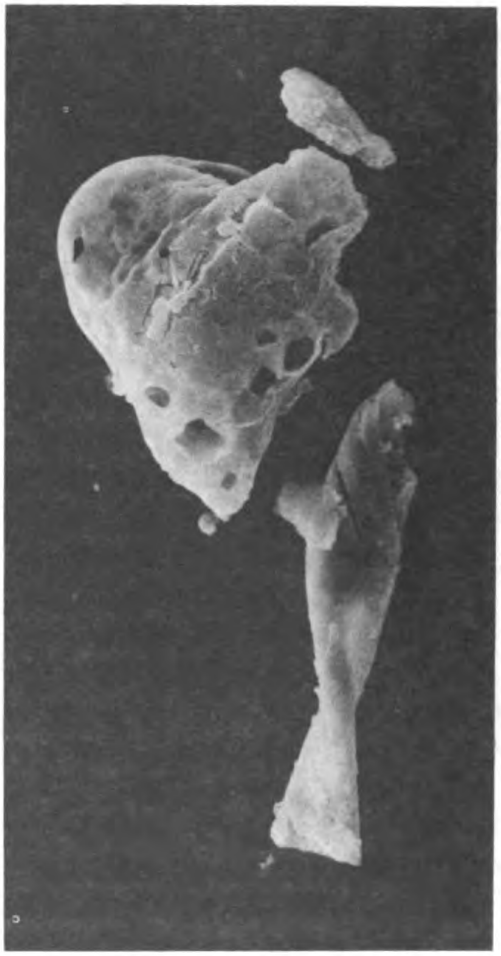

*Figure 10b — Unknown particles.*

*Figure 10 — Ferrogram of synovial fluid from an arthritic patient. These Scanning Electron Micrographs reveal the complexity of some particles in the synovial fluid. It is too early to properly classify the kinds of particles and their source. Hundreds of samples will have to be analyzed first. However, several materials have been identified by preparing Ferrograms containing particles from known sources such as bone, cartilage, etc.*

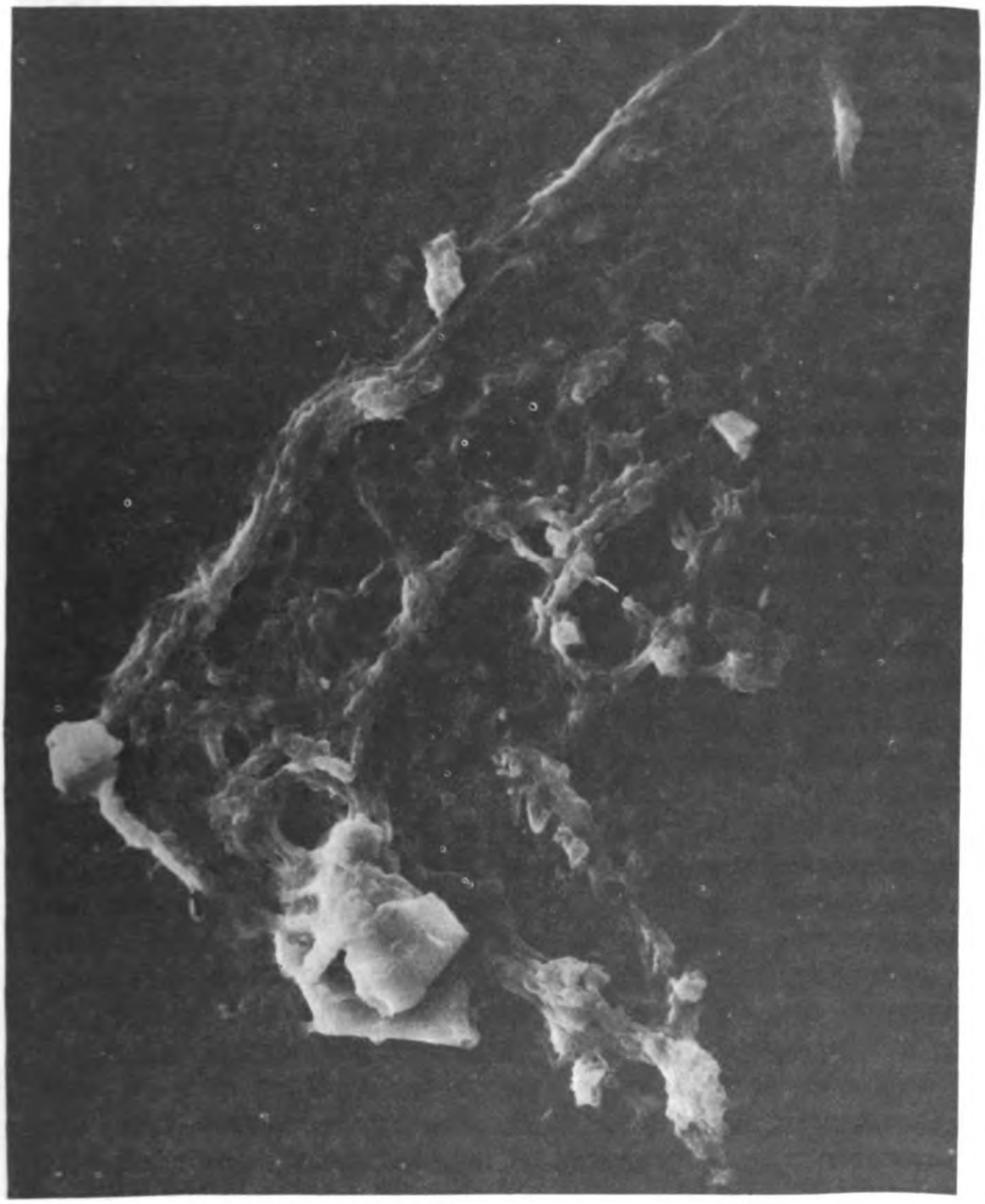

*Figure 10c — Tissue containing cartilage (white area).*

***Figure 10 (Continued) — Ferrogram of synovial fluid from an arthritic patient. These Scanning Electron Micrographs reveal the complexity of some particles in the synovial fluid. It is too early to properly classify the kinds of particles and their source. Hundreds of samples will have to be analyzed first. However, several materials have been identified by preparing Ferrograms containing particles from known sources such as bone, cartilage, etc.***

Since then a variety of man made plastics, as well as plant and animal tissues have been precipitated and it appears that the Ferrographic technique can be extended to the recovery of all materials. Even living bacteria have been recovered. We are looking forward to using this versatile technique as a field and research tool for studying a variety of systems from diesel engines to human joints by recovering particles ranging from the steel fatigue particles of gears to tiny bacteria in fluid systems. Perhaps the science of Ferrography is in its turn entering upon new and expanding territory.

(The author wishes to thank the Advanced Research Projects Agency of the U.S. Department of Defense, Materials Sciences Section, Dr. Edward van Reuth, Project Manager, for support of research leading to an understanding of the relationship between the particles of wear and the mechanism of their generation as well as the development of techniques of particle identification. The program is monitored by the Office of Naval Research, Dr. Richard Miller and Lt. Commander Kirk Petrovic, Scientific Officers.

The investigation of Ferrogram particle distribution and the analysis of the composition and crystallographic order of individual particles carried out at the National Bureau of Standards under Dr. A. W. Ruff has provided fundamental information on the interpretation of Ferrograms.

We wish to express our appreciation for the help and advice of many investigators in the U.S. and Europe including Mr. Douglas Scott of the National Engineering Laboratory, Scotland, and Dr. Frederick Barwell, University College of Swansea, Wales.

The Naval Air System Command, Mr. Bernard Poppert, through the Naval Air Engineering Center, Mr. Peter Senholzi, Research Group Leader, has funded a series of contracts with various organizations which have contributed knowledge and experience about how various mechanical parts generate wear particles. An Atlas of wear particles is being prepared as part of this program, the first sections of which have been completed.)

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*30th Anniversary Article*

# An Overview of Hydrogen Failure Mechanisms

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## Introduction

The recognition of hydrogen as a ubiquitous and generally deleterious solute in metallic systems dates to the mid-nineteenth century when W. H. Johnson (1) observed and reported on most of the general phenomena of hydrogen embrittlement of steels. Since that time these observations have been extended to a wide range of metallic systems both ferrous and non-ferrous, and the role of hydrogen in inducing brittle failure has been widely recognized. As a result, the phenomena associated with hydrogen effects are well characterized; and as we will describe, a remarkable generality of behavior can be noted. Much of the work in this area and the understanding of this problem has resulted from programs supported by the Office of Naval Research. Recognizing the role of hydrogen in many engineering failures, ONR sponsored programs to both increase the basic understanding of this class of failures as well as to develop methods of avoiding them. In large measure, these programs have been successful.

The subject of hydrogen induced failures remains an exciting research area, and new phenomena are still being discovered. Systems, such as Al, Mo, and W alloys, which were previously considered to be "immune", have been recently shown to be subject to hydrogen embrittlement under the proper conditions. A particular objective of many studies has been the understanding of the mechanism of the hydrogen induced failures, and in this the studies have been only partially successful. The thrust towards a mechanistic understanding has been

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motivated in part by an attempt to establish a general mechanism which would account for the behavior of all systems; an optimistic goal which does not appear to be valid. Recent progress towards a mechanistic understanding has been made, and the status of this knowledge will be summarized. The utility of such understanding is that it can (a) suggest practical steps which can be taken to minimize the deleterious effects of hydrogen, (b) delineate the service conditions under which hydrogen effects are most severe, and (c) determine applications of materials for which no remedy for the hydrogen problems exist and which therefore should be avoided.

## Classification Schemes

In examining the effects of hydrogen on the mechanical properties of metals it is useful to classify the systems according to several different schemes. One such classification can be based on the stability of hydrides; which for the purpose of this discussion will be considered as phases which are generally centered around stochiometric H/metal ratios and have an ordered arrangement of H atoms. The hydrides formed in metallic systems have a variety of types of bonding ranging from metallic to ionic, exist over appreciable ranges of H/metal ratios, and generally do not require diffusive motion of the metal atoms during their formation (2). While most hydrides form by first order phase changes, they can result from low temperature ordering reactions. In hydride forming systems (such as Nb, V, Ti, Zr, Mg) there is increasing evidence that the hydrogen embrittlement is closely related to hydride formation. Metallic systems which do not form stable hydrides (such as Fe, Mn, W, Mo) also show extreme susceptibility to hydrogen induced failure and in these cases the experimental evidence suggests a failure mechanism based on a hydrogen related decrease in atomic bond energy. In a number of systems, such as Ni-H, the hydride has marginal stability and its role in the embrittlement process is not clear.

Another useful classification may be based on the heat of solution of H in the metal in equilibrium with the gas phase (2). Since this parameter determines whether the solid solution can become supersaturated with respect to the gas phase on cooling the alloy, it is of interest with regard to the formation of high pressure gas filled bubbles. Thus systems which have endothermic heats of solution (Fe, Mo, Al, Ni, Mg) are susceptible to failures initiated by precipitation of a high pressure gas phase whereas systems having exothermic heats of solution (Ti, Nb, V, Zr) are not. It may also be noted that the magnitude of the H solubility is much greater in systems which have exothermic heats of solutions, and that these systems generally form stable hydrides. However, a number of systems which exhibit endothermic heats of solution, such as Al, Mg, and Ni also form hydrides under suitable conditions.

As will be discussed shortly, the hydrogen related failures generally require the accumulation of hydrogen at particular points in the structure; a requirement which leads to a classification based on the source of the hydrogen. Thus hydrogen present in solid solution (internal hydrogen) must diffuse to a crack tip while hydrogen from a gas atmosphere or a corrosion reaction (external hydrogen) is generall available at the crack tip, albeit in a form which may require the overcoming of an adsorption or surface diffusion barrier. Thus the kinetics of the failure process can be expected to depend on the hydrogen source even though the mechanisms may not. The distinction between "internal hydrogen" and "external hydrogen" failures, while often made, is of little consequence with regard to failure mechanisms.

## General Failure Characteristics

The general characteristics of hydrogen related failures appear to be similar in many systems, and it is this similarity that has motivated attempts to develop a single failure mechanism. In this section we will briefly review those general patterns which describe the behavior of metallic systems in the presence of internal or external hydrogen (3,4,5).

As shown in Figure 1 the strain to failure in a tension test exhibits a ductility minimum which characteristically falls below 300°K. The nature of the fracture surface reflects the ductile - brittle - ductile transitions as ductile failure modes (shear or microvoid coalesence) predominate, except at the ductility minimum where fracture occurs by a brittle mode. In this latter range, hydride forming systems exhibit transgranular cleavage while the non-hydride forming systems fracture by intercrystalline failure along grain broundaries or prior austenitic boundaries in steels. Under suitable conditions, hydrogen induced fracture of stainless steels or high strength aluminum alloys can occur either by transgranular cleavage or intercrystalline brittle fracture. In general, the failure mode depends primarily on the system but may vary with the hydrogen source or loading procedure in some systems. The temperature of the ductile - brittle transition depends on the system, testing mode, and on the hydrogen concentration. In hydride forming systems, the decrease of ductility occurs at temperatures higher than but correlated with the hydride solvus temperature.

The temperatures of these fracture transitions and the magnitude of the ductility decrease are sensitive to the applied strain rate; the ductility increasing as the strain rate increases (Figure 1). This inverse strain rate sensitivity and the return of ductility at low temperatures are manifestations of the kinetics of the embrittlement and reflect the diffusivity of hydrogen.

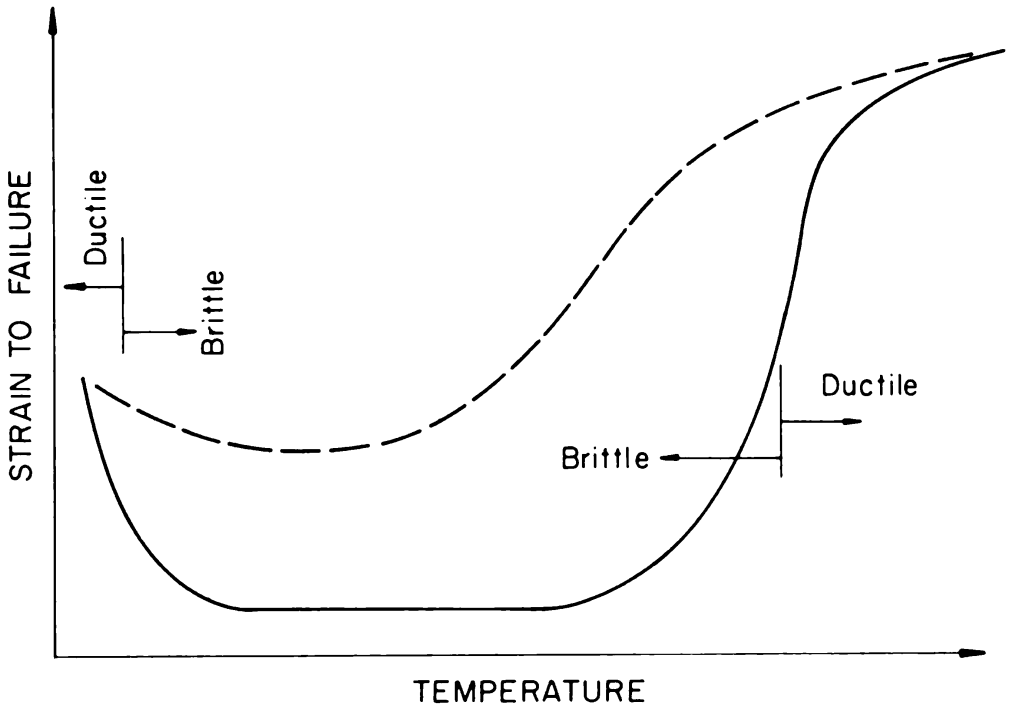



*Figure 1 – Variation of ductility with temperature for metal-hydrogen systems. As the temperature is decreased the fracture surface exhibits a ductile - brittle - ductile transition. ——— low strain rates; - - - high strain rates.*

The dependence of the ductility decrease temperature on hydrogen concentration for non-hydride forming systems has not been well established but the transition temperatures appear to increase with hydrogen concentration. A particularly interesting question, which has not be examined, is whether the ductile - brittle transition temperature correlates with the hydrogen diffusivity. At each temperature in the ductility minimum, the stress at which brittle fracture occurs decreases as the hydrogen concentration increases (Figure 2). Even at hydrogen concentrations of the order of one part per million, brittle fracture occurs in ferrous systems. There does not appear to be a threshold concentration below which high strength steels are immune to hydrogen related fracture.

A characteristic behavior of the ferrous (b.c.c.) - hydrogen systems is static fatigue (Figure 3). In these systems the brittle fracture occurs after a period of time at constant stress. The delay time consists of an initial period where the hydrogen damage is reversible followed by irreversible crack nucleation and growth. Removal of the solute hydrogen by vacuum annealing prior to crack nucleation leads to complete restoration of the specimen ductility whereas, once the cracks form, an irreversible effect which depends on the notch sensitivity of the alloy is present. Once again the kinetics of these processes reflect the kinetics

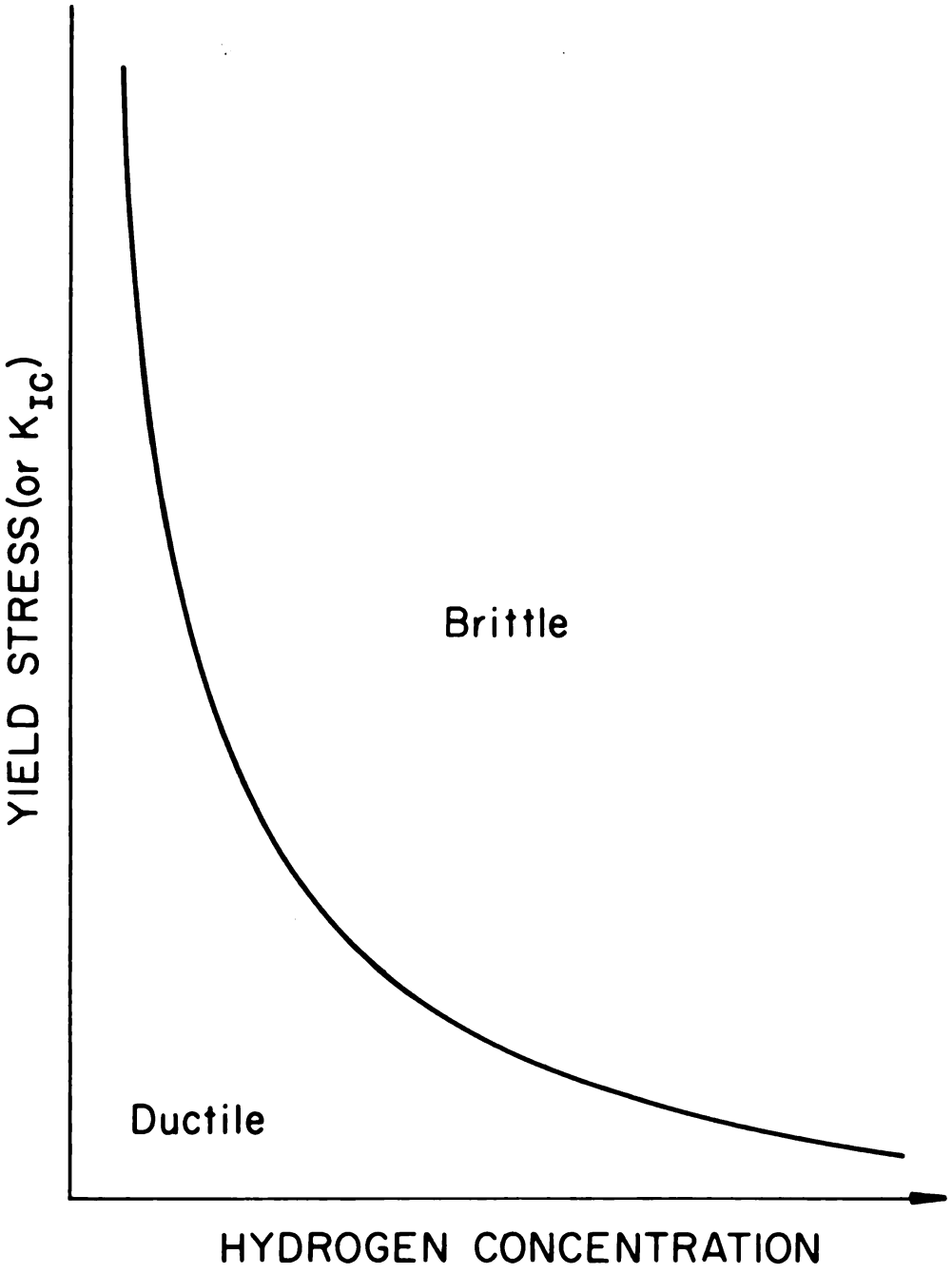



*Figure 2 – Dependence of the stress for fracture (or the critical stress intensity $K_{IC}$) on the concentration of hydrogen.*

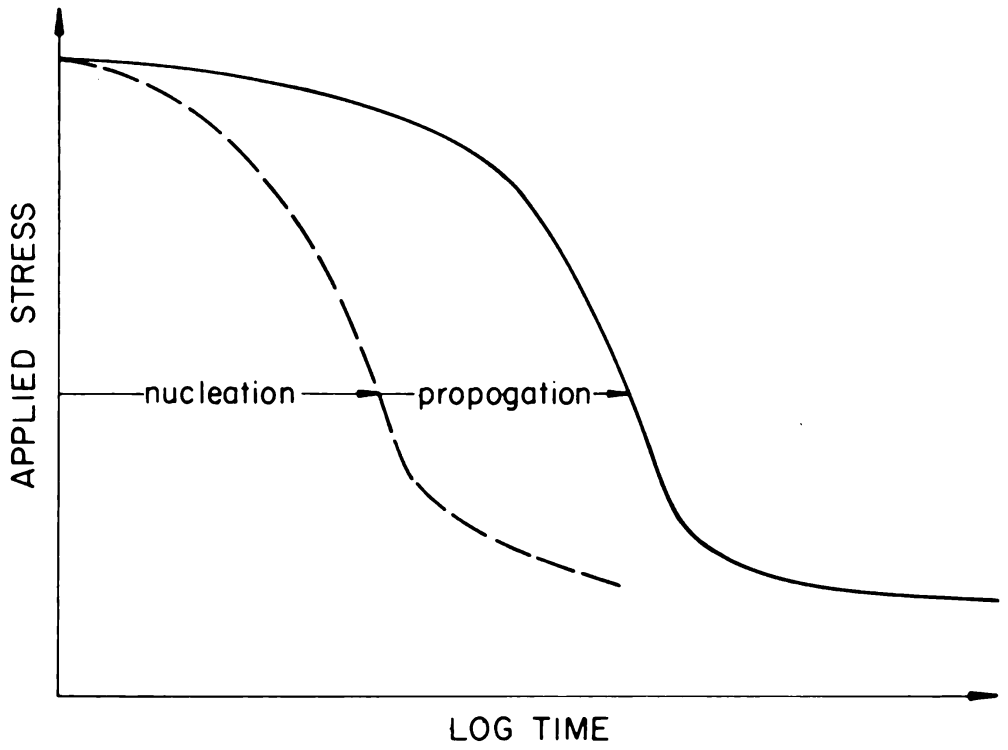



*Figure 3 — Static fatigue behavior of metal - hydrogen systems. ——— time to fractures vs. the applied stress - - - time to initiate a crack vs. the applied stress.*

of hydrogen diffusion as well as the source of the hydrogen, internal or external. Delayed fatigue has not been reported in hydride forming systems but it should occur under suitable conditions.

No general conclusions can be drawn concerning the fracture paths for hydrogen related brittle fracture. These seem to depend on whether the system is a hydride former or not, on the source of hydrogen, and on the metallurgical structure. Single phase hydride forming systems exhibit transgranular cleavage on a plane which is consistent with the hydride cleavage plane. If second phase precipitated hydrides are present, these act as fracture initiation sites and multiple cracks result. Even in the absence of precipitated hydrides, extensive secondary cracking is usually observed. In two phase hydride forming alloys, such as $\alpha - \beta$ Widmanstatten Ti alloys, the cracks often propagate along the phase boundaries. This situation is complicated by the fact that the hydrogen solvus often differs greatly in the two phases as does the hydride stability and the hydrogen diffusivity. It appears that the $\beta$ phase acts as a high diffusivity path and that the fracture actually takes place in the $\alpha$ phase.

Non-hydride forming alloys generally exhibit hydrogen induced intercrystalline brittle fracture. In single phase nickel alloys the fracture initiates and propagates along grain boundaries while in high strength

steels the fracture proceeds along prior austenitic boundaries. With respect to the fracture path in these alloys, the effect of hydrogen is similar to that of other elements such as P, S, As, etc. which cause temper embrittlement. In type 304 austenitic stainless steels the hydrogen induced fracture proceeds by transgranular cleavage when tested in $H_2$ gas at slow strain rates. In this case $\alpha'$ martensite is formed along the fracture surface either prior to or during the crack propagation. The role of this martensite phase transition in the fracture process is not established but it may provide either a high diffusivity path or a phase more susceptible to embrittlement than the austenite.

The classical cases of hydrogen embrittlement are associated with internal (solute) or external (gaseous) hydrogen. In recent years, however, an increasing amount of experimental data suggests that stress corrosion failures in environments which produce hydrogen at the crack tip are often related to hydrogen embrittlement (6). Evidence for this correlation has been established in hydride forming alloys of titanium and magnesium and in high strength aluminum age hardening alloys as well as for austenitic stainless steels. The connection between stress corrosion and hydrogen embrittlement remains a very controversial topic, and in no case has more than a circumstantial connection been made. The basis for this correlation is primarily morphological and fractographic similarities between the two types of fracture. In high strength aluminum age hardening alloys intergranular brittle crack propagation has been observed during stress corrosion after cathodically charging and after exposure to moist air. The similarity of the fracture surfaces and the presence of what appears to be a brittle film along the surface has led to the suggestion of fracture due to the formation of a brittle aluminum hydride in all three cases. In contrast to these observations, the formation of small hydrogen gas filled bubbles has also been observed in front of a propagating stress corrosion crack. Thus while the failure mechanism is in some dispute, increasing evidence for the involvement of hydrogen in stress corrosion of aluminum alloys exists. A similar situation appears to be developing for the stainless steels which were thought to be "immune" to hydrogen induced fracture but were susceptible to stress corrosion cracking. Type 304 austenitic stainless steels have been shown to exhibit slow crack growth by transgranular cleavage in one atmosphere of $H_2$ gas or while being cathodically polarized. Most stable austenitic stainless steels such as 310 do not exhibit this type of failure.

In many respects the fracture behavior appears to be independent of the hydrogen source: internal or external, gaseous or corrosion product. The source of hydrogen primarily affects the kinetics of the embrittlement process since the hydrogen must be present at the crack tip; at a specific position which depends on the detailed mechanism.

Internal hydrogen requires either hydrogen diffusion (7) or a dislocation transport mechanism (8) to reach the crack tip. As a result, the static fatigue behavior can be understood as a manifestation of the transport kinetics, and its temperature dependence reflects that a diffusion or dislocation dragging. In those systems where hydrogen diffusion rates are low (Mo, W, Al) it is not possible to bring sufficient hydrogen to the stress concentrations, and hydrogen embrittlement does not occur. A similar explanation can account for the return of ductility at low temperatures where the diffusivity decreases.

Systems having low hydrogen diffusivity do exhibit embrittlement under conditions where the hydrogen is produced at the crack tip. Thus systems such as Mo and W alloys and 304 stainless steels are embrittled by cathodic charging during tension tests, and stress corrosion cracking appears to be related to hydrogen evolution at the crack tip. Many of the systems which exhibit embrittlement under stress corrosion or internal hydrogen conditions also fail when tested in gaseous hydrogen or aggressive hydrogen containing atmospheres ($H_2S$ for example). Under both stress corrosion and gaseous hydrogen conditions the failure kinetics are often limited by transfer of hydrogen across the solid surface. Since this involves several processes, each of which may be rate limiting, the kinetics are often complicated and are poorly understood.

The behaviors discussed above reflect the influence of hydrogen on the brittle fracture of solids under external stresses. Unfortunately, this is only one aspect of the problem as hydrogen also affects the ductile fracture process of many alloys (9). Thus, even in those systems which retain their ductile failure behavior in the presence of hydrogen, a drastic decrease in the strain to failure and therefore in the "toughness" can occur. These effects on ductile fracture are most pronounced in alloy systems having a positive heat of solution of hydrogen and are associated with the nucleation and growth of microvoids. In some cases these effects can be related to a hydrogen caused decrease in interfacial cohesion at second phase particles and to the formation of high pressure gas bubbles in equilibrium with the supersaturated solid solutions. This type of reduced ductile fracture strain in a tensile test has been reported in a variety of austenitic stainless steels, such as types 304, 310 and 21-6-9, after cathodic charging. Extensive surface cracking and transformation to martensite (for type 304) is also observed in these specimens as a result of the severe hydrogen charging and the attendent surface strains.

A further deleterious effect caused by hydrogen often results from the high temperature reaction of solute hydrogen with other solutes such as O or C or with precipitated oxides or carbides (10). Exposure of steels to high pressure hydrogen at temperatures of the order of 300

to 500°C leads to a drastic decrease of strength and ductility after a period of exposure during which little effect is found. These effects are associated with the formation of methane bubbles along grain boundaries. A similar behavior has been observed on annealing non-ferrous alloys containing high O solute concentrations in hydrogen atmospheres. In these cases high pressure $H_20$ gas bubbles are formed.

## Embrittlement Mechanisms

### Hydride Forming Systems

The "low temperature" fracture mechanism in these systems appears to be clearly related to the formation of second phase hydrides which provide both crack nucleii and fracture paths. Support for this mechanism is based on in-situ S. E. M. fracture studies, T. E. M. studies, ion probe studies and thermodynamic considerations (11).

Hydrides are generally extremely brittle phases and exhibit cleavage on well defined planes. A volume increase of about 10% typically accompanies the hydride formation from the solid solution and this is accommodated by elastic strain and by severe deformation in the matrix around the hydrides. Thus cooling these systems into the two phase regions or exposing them to an external hydrogen fugacity, which is sufficiently large to form the hydride, results in the formation of a highly stressed distributed brittle second phase. Hydride precipitation from solid solution does not generally form as a continuous phase but rather as discrete brittle particles which crack under external stress and provide multiple crack nucleii from which fracture propagates. In the case of external hydrogen, a surface hydride phase may form and provide the crack nucleus by cleaving under stress exposing fresh metal for further hydride formation. Thus, for external hydrogen of sufficiently high fugacity, the crack propagates through hydride forming at its tip and at a rate which is determined by the transfer of hydrogen across the gas-solid interface to the region in front of the crack where the highest triaxial stress exists. The entry of hydrogen and therefore the crack propagation rate may be limited by surface processes as many of these systems, such as the Group Va metals, form extremely stable oxides which act as permeation barriers at low temperatures.

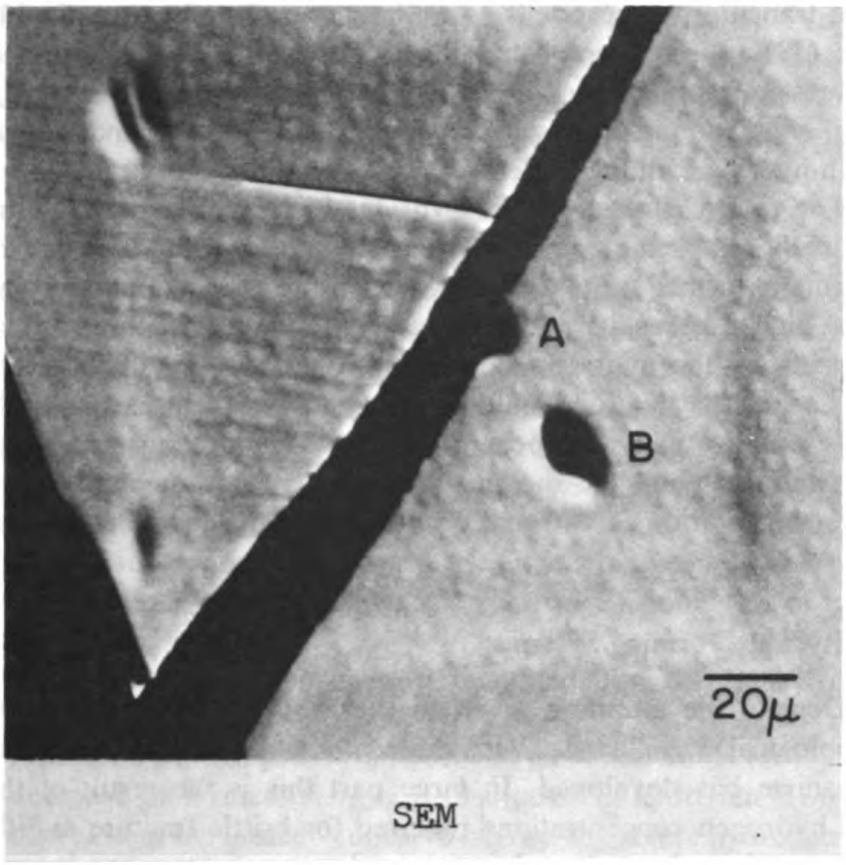
Internal hydrogen induced fracture requires crack propagation from the precipitated hydrides which nucleate the cracks. The dilitation field at the crack tip reduces the chemical potential of the solute hydrogen producing flux proportional to the hydrogen diffusivity in the crack tip stress field. The chemical potential of the hydride is also reduced by the crack tip stress field due to the volume expansion associated with the transformation of the solid solution to the hydride.

This latter effect leads to a tendency for continued hydride formation at the crack tip. In many systems (such as the group Va metals) the hydride can form by ordering of the hydrogen on a subset of the interstitial sites, and only elastic displacements of the metal atoms are required. In these cases the hydride precipitation is limited only by hydrogen diffusion and can take place at very low temperatures. Propagation of the cracks in these systems occurs by the formation of hydride at the crack tip followed by cleavage and at a rate determined by hydrogen diffusion to the crack tip (11) (Figure 4). The dependence of the crack propagation rate on hydrogen diffusion to the crack tip or transport across the gas-solid interface can account for the brittle to ductile transition which is observed as the temperature is decreased or the strain rate increased. A similar dependence can account for the greater ductility observed in the presence of deuterium rather than hydrogen.

In other systems, such as the zirconium alloys, hydride formation requires rearrangement of the metal atoms either by diffusion or by correlated shears. In these cases the rate of hydride formation at the crack tip may be limited by the precipitation process rather than by hydrogen diffusion. At elevated temperatures and low strain rates the hydride formation rate may be rapid enough to allow propagation by hydride formation and cleavage. At lower temperatures or higher strain rates the hydride formation rate may not be sufficient and failure will occur by ductile rupture of the alloy between the hydrides precipitated prior to the test.

Hydride formation and cleavage can occur at temperatures and concentrations at which precipitation does not normally occur in the absence of stress (12). Reduction of the chemical potential of the hydride phase by application of a suitable external stress can result in a significant increase in the hydride solvus temperature. Stress induced hydride precipitation followed by crack nucleation and propagation through the hydride phase and the resulting ductile-brittle transition will therefore occur at temperatures above the stress-free hydride solvus temperature. The extent of this upward temperature shift is determined by the applied stress and consequently strengthening of the alloy will generally result in an upwards shift of the ductile-brittle transition.

A recent series of observations have shown that "high temperature" hydrogen induced cleavage can occur in some of the hydride forming systems. These failures appear to occur at a critical hydrogen concentration and in a region of the phase diagram where second phase hydrides cannot form, even under stress. This type of failure, which occurs at relatively high hydrogen concentrations, does appear to be associated with a stress induced phase separation into a random solid solution, $\alpha$, which is ductile, and a "locally ordered" solid solution, $\alpha'$, which is brittle and fails by cleavage. The $\alpha \rightarrow \alpha'$ stress induced

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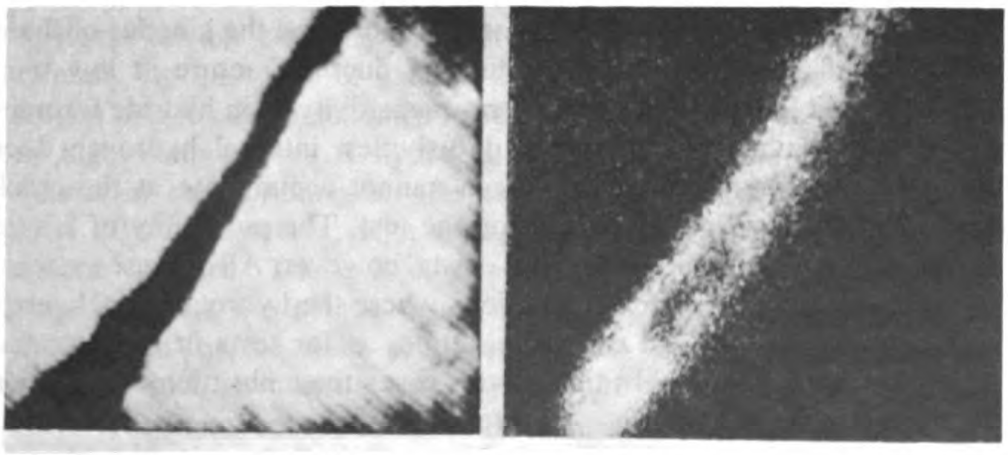


B C

*Figure 4 — Images of a hydrogen embrittlement crack in a Nb - H alloy. (a) scanning electron microscope image (b) secondary ion mass spectrometer (ion probe) image using mass 93, $Nb^+$ (c) ion probe image using mass 94 $NbH^+$. The distribution of $NbH^+$ intensity indicates that NbH hydride is formed along the fracture surface.*

phase transition corresponds to a "lattice gas" → "lattice liquid" transition (13). A basic understanding of the nature of this transition and its effect on fracture is not yet available. It is also not known how general this phenomenon is or how it is related to the hydrogen induced fracture of non-hydride forming systems.

The role of stress induced hydrides in systems where hydrides are marginally stable is very poorly understood. While nickel hydride is normally formed only at high hydrogen fugacities, it may be stabilized by the high stresses at crack tips and cause brittle fracture. Propagation of cracks by the hydride mechanism would be difficult to establish in this case, as the hydride would be stable only in the presence of the high stresses and would disappear after the crack propagated, a veritable "Maxwell Demon". A similar situation may pertain in the Al alloys where the hydride is extremely unstable in the presence of traces of $H_2O$.

**Non-Hydride Forming Systems**

Despite the attention given to these systems as a result of their technological significance very little understanding of their fracture mechanism has developed. In large part this is the result of the very small hydrogen concentrations required for brittle fracture and the lack of information about the effects these low concentrations have on the lattice properties. As discussed previously, the fracture phenomena suggest that hydrogen must be present at the crack tip in order to induce fracture. In the case of internal hydrogen, the transport to the crack tip may be by diffusion or dislocation transport, and the kinetics of these processes can account for the return of ductile fracture at low temperatures and for the inverse strain rate sensitivity as in hydride formers. In systems having low hydrogen diffusivities, internal hydrogen does not cause embrittlement as hydrogen cannot accumulate at the crack tip in sufficient concentration during the test. The possibility of failure under sustained load (static fatigue) exists, however. All of these systems exhibit embrittlement under conditions where the hydrogen is delivered at the crack tip and can enter the lattice, as for tests in gaseous and corrosion environments. In these latter cases the embrittlement kinetics can be determined by surface transfer processes.

In these systems the chemical potential of the solute hydrogen can be reduced by the crack tip stresses and the resultant flux of hydrogen can increase the local concentration by a factor of less than $10^2$. Thus even under the most favorable stress conditions, embrittlement occurs at crack tip concentration levels of the order of 100 ppm (atomic). Nonetheless the fracture properties of this very dilute solution are drastically altered. At these concentration levels there is no evidence

for significant effects on the plastic properties of the solution. Fracture appears to occur when a critical hydrogen concentration is attained at each stress and temperature, and in a gaseous hydrogen atmosphere this corresponds to a critical hydrogen gas pressure for crack propagation (14).

The hydrogen induced fracture paths are often observed to be along interfaces such as grain boundaries, second phase interfaces or prior austenitic boundaries in steels as is observed in other types of impurity induced embrittlement, such as temper embrittlement. In the absence of such boundaries the hydrogen induced fracture proceeds by transgranular cleavage. We shall adopt the point of view that the intergranular brittle fracture and transgranular cleavage are basically the same process; but that the fracture follows the paths of greatest weakness, which generally are interfaces in alloys such as steels. This point of view also suggests that synergistic effects between those solutes which cause temper embrittlement and hydrogen should be of great importance in steels.

The embrittlement mechanisms proposed for the non-hydride forming systems include:

(a) formation of high pressure hydrogen gas filled voids (15)
(b) decrease of surface energy by adsorption of hydrogen (16)
(c) decrease of the lattice "cohesive energy" by solute hydrogen (17)
(d) hydrogen induced changes in the plastic properties at the crack tip leading to decreased toughness and increased notch sensitivity (18).

Mechanism (a) is known to cause "blistering" and "fissures" in systems having endothermic heats of solution such as steels and aluminum. In this type of system a supersaturated concentration of hydrogen can result on solidification from welding or on cooling rapidly from high temperatures if hydrogen or water vapor is present. The pressures in equilibrium with the supersaturated solutions can be as high as $10^5$ atmospheres; high enough to cause bubble formation and attendant fracture. These high effective pressures can provide the driving force for the plastic processes which accompany the bubble formation and for the crack propagation from the bubbles. The mechanism by which the brittle cracks propagate from the high pressure bubbles still must be determined. Brittle crack propagation has also been observed in high strength steels at hydrogen gas pressures of one atmosphere and below. Since the effective internal pressures must be less than or equal to the external pressures, fracture under low pressure hydrogen cannot be due to bubble formation.

Hydrogen has been observed to have little effect on the yield stress or work hardening rates of metals in the temperature ranges where embrittlement is observed. Even in the Ni-H system, where

hydrogen related yield points and Portevin-Le Chatalier effects are observed at low temperatures, the hydrogen induced brittle fracture occurs at temperatures where these effects are absent. Thus mechanism (d) does not appear to be related to hydrogen induced brittle fracture although it may be a significance in cases of ductile failure by microvoid coalescence. The primary role of crack tip plasticity in brittle failures appears to be in determining the stress intensity and possibly in providing an enhanced hydrogen transport mechanism by dislocation dragging.

The original proposal by Petch (19) that hydrogen reduces the fracture stress due to adsorption on the fracture surfaces (mechanism (b)) is clearly not viable as other atmospheres such as oxygen, nitrogen or water vapor which adsorb on clean surfaces even more strongly than $H_2$ do not cause fracture. A consideration of the energy balance during fracture does suggest, however, that the fracture stress would be reduced if hydrogen were to decrease the energy to form the two surfaces by decreasing the cohesive forces between atoms (16). Thus, since the surface energy and cohesive energy of a solid are closely related, recent interpretations have seen a blending of mechanisms (b) and (c). Oriani (17) has formalized an original suggestion by Troiano that hydrogen decreases the cohesive energy of the solid as well as the cohesive force between atoms. As a consequence of this approach, fracture occurs when the force between atoms exceeds the hydrogen reduced cohesive force. Since the hydrogen concentration at the crack tip is in equilibrium with solute hydrogen or the hydrogen pressure in the gas phase, cleavage failure occurs at a stress intensity which decreases with increases in solute hydrogen concentration or with external hydrogen gas pressure. Although this concept can account for most of the experimental observations, the functional dependence of the cohesive force on the local hydrogen concentration is not known. Measurement of the elastic constants of b.c.c. metals do not indicate that they (and therefore the curvature of the lattice potential at the equilibrium atomic spacing) depend sensitively on the hydrogen concentration. Indeed even the signs of the change of the constants with hydrogen concentrations are not consistent in the different metals. Neutron diffraction studies of the effects of hydrogen on the phonon dispersion curves have been carried out on a few systems, and these do not indicate a great sensitivity to the presence of hydrogen. A survey of the hydrogen dependence of various phonon and electronic properties of the b.c.c. metals suggests that while these do depend on hydrogen concentration, the changes are not sufficiently large to account for ductile to brittle transition observed at very low hydrogen concentrations. Unfortunately, the hydrogen solubilities in the non-hydride forming systems are so low that measurements such as hydrogen effects on phonon dispersion

curves cannot be carried out. For the present therefore, the postulate on which mechanisms (b) and (c) are based cannot be proven.

## Summary

A review of the available information on hydrogen effects allows us to draw a number of conclusions, some of which must be rather tentative at the present time. These may be summarized as:

(1) Hydrogen embrittlement occurs under conditions where the source of hydrogen is solute hydrogen, a gaseous hydrogen atmosphere, or a corrosion environment. Differences in behavior between these various sources are reflected primarily in the kinetics of the fracture process as it is necessary for the hydrogen to be present at the crack tip in order that fracture be caused.

(2) A critical hydrogen concentration, which is a function of the applied stress intensity, appears to be necessary for the transition from a ductile to a brittle fracture mode. In hydride forming systems this concentration corresponds to the formation of a brittle hydride phase which serves to nucleate the crack and through which the fracture propagates. In non-hydride forming systems this critical concentration is *postulated* to reduce the lattice cohesive force to a value less than that applied by the external stress.

(3) The kinetics of crack propagation reflect the transport of hydrogen to the crack tip. The decreased flux at low temperatures can account for the brittle - ductile transition as the temperature is decreased or the strain rate increased.

(4) The primary effect of plastic processes is on the crack tip stress intensity and therefore on the temperature at which hydride can form or on the critical hydrogen concentration for lattice decohesion.

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## New Power Supply

A newly developed electronic power supply unit is expected to offer big dividends for Navy and industrial equipment where systems require portable, highly versatile power conditioners. Intended for use from any voltage from 12 volts to 300 volts, the power supply will operate with either AC or DC. A prime advantage of this power supply is that it converts a wide range of AC and DC voltages to suit the voltage requirements of any particular device.

Besides being used in aircraft, missiles and submarines, the power supply could be used to power digital clocks, engine alarm systems, communications and safety devices, and automatic pilots for aircraft.

This wide-range input power supply has been designed, developed and operated by the Naval Electronics Laboratory Center (NELC) in San Diego.

Applications for a power supply of this type, which acts as a common denominator or coupler, include nearly every piece of electronic equipment and electronic device which must have a power conditioner. With the regulated, reliable output provided by this unit, widely fluctuating input voltage will no longer cause a problem. Its universal characteristic permits the unit to fit about 90 percent of all the power sources that the Navy uses. Weighing as little as four-ounces and measuring approximately 2" × 2" × 3", the unit can power electronic systems for 115,000 hours mean time between failure, or approximately 12 years. The power supply's weight, size, efficiency and versatility (operates with either AC or DC in any voltage from 12 to 300 units) gives the power supply important advantages over other power supplies that are commercially available.

# Research Notes

## Large Radiotelescope

Radio astronomers at the Naval Research Laboratory (NRL) have joined with colleagues in California, Australia, and the USSR to put together an enormous radiotelescope the size of the earth.

Large radio telescopes near NRL, in California, Australia and the USSR were linked to form the huge resultant antenna which, effectively, has the resolving power of a radiotelescope the size of the earth and the capability of resolving a source less than 2 ten thousandths of a second of arc, comparable to the thickness of a human hair at a distance of 100 miles or a man's footprint on the moon.

A radiotelescope of this size is required to study primordial clouds containing water vapor out of which new stars are being formed in distant regions of our galaxy. These water molecules produce extremely intense radio radiation by maser amplification, analogous to the mechanism of optical lasers.

The four large radiotelescopes distributed around the world were joined together by using the technique of Very Long Baseline Interferometry (VLBI) to get the highest angular resolving power ever achieved at radio frequencies.

This technique consists of recording the signals received at each antenna on video tape and later comparing the recordings. When the recordings are matched, the size of the source is determined with a precision comparable to the resolving power of an antenna of size equal to the separation between the two antennas.

The antennas used in this experiment were the 85-foot antenna of NRL's Maryland Point Observatory at Maryland Point, Maryland, the 210-foot antenna of NASA's Deep Space Network (DSN) at Tidbinbilla, Australia, the 72-foot antenna of the Crimean Astrophysical Observatory at Semeiz, USSR, and the 130-foot antenna of the California Institute of Technology at Owns Valley, California.

The maximum spacing achievable is the earth's diameter, 12,600 km. The separation of the NRL antenna at Maryland Point and the NASA DSN antenna at Tidbinbilla is very close to this limit, being separated by 12,091 km.

The high angular resolution was essential to distinguish details of the spatial structure of clouds of molecular water vapor in our galaxy. These clouds are so bright that the impossible temperature of $10^{13}$ degrees K would be needed to generate the emission by ordinary processes. Scientists believe these sources are natural masers. Maser is an acronym for Microwave Amplification by Stimulated Emission of Radiation.

The most intense radiation in the masing water vapor spectrum of one of these sources, named W49N, appears as intense as the sun at the same frequency. This source is about three billion times as far from the earth as the sun is, making it an extremely energetic object.

The water vapor masers are believed to be associated with the process of star formation that takes place in giant clouds in our galaxy. These high angular resolution studies allow one to measure the size and shape of the individual masers and their distribution within the cloud.

The masing radiation permits one to look deep into these clouds that heavily obscure radiation at other frequencies, enabling estimates to be made of the physical conditions that give rise to star formation.

Signals from the strong water maser, W49N and W51, were recorded on video tape at precisely the same time when the radio sources were mutually visible above the horizon of two of the antennas. These two sources are commonly visible at Maryland Point and Tidbinbilla for about an hour each day.

A day's observation consisted of first observing the sources over the transatlantic baseline between Crimea and the US, i.e. between Semeiz and Maryland Point, next across the US between Maryland Point and Owens Valley, then across the Pacific between Maryland Point, Owens Valley, and Tidbinbilla, and finally between Tidbinbilla and Semeiz.

The signals from the $H_20$ masers received at the telescopes were recorded on video tape at a bandwidth of 2 MHz.

The signals recorded on the tape must have a frequency stability of a fraction of their wavelength in order to be compared. The wavelength of the masing water molecule is 1.34 cm, requiring the frequency stability of the recording to exceed one part in a trillion ($10^{12}$).

In order to achieve this, the scientists at each telescope had to use hydrogen maser frequency standards to tune the $H_20$ masing signal down in frequency in order to record it. These frequency standards derive their stability from a transition of neutral hydrogen atom at 1,420 MHz and are the most accurate clocks that man can devise. They are correct to about one second in a million years.

The spatial structure of the $H_20$ molecular masers was found to be very complex. The recorded signals from the masers displayed varying correlations with time and over the different baselines. The sizes of the individual masing sources, which may exceed 100 in number in a single cloud, were found to range from half to three times the distance between the earth and sun.

The masers appear to be in clumps in the source W49N, indicating that several stars have formed simultaneously in this cloud. The data resulting from this experiment is now being analyzed in order to make more detailed models of the size and shapes of these masing molecular clouds.

## Radiative Charge Transfer Studies

Professor John Weiner Dartmouth College, has measured radiative charge transfer cross sections for the reactions between alkali ions and various molecular gases. A beam of alkali ions ($Li^+$, $Na^+$, $K^+$, $Rb^+$ and $Cs^+$) is produced by a tungsten surface ionization source and electrostatically focused into a well defined interaction region. Neutral gas is then bled into the vacuum chamber and photon emission rates arising from the ion-gas-interaction are measured with a monochrometer and a photomultiplier tube detector.





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These radiative charge transfer processes, as, for example, $Na^+ + CO_2 \rightarrow Na^*(3p) + CO_2^+$, where the emission comes from the excited $Na^*(3p)$ state decaying to the Na (3S) ground state, are very important for several reasons. First, these experiments measure absolute cross sections for charge transfer into specific excited states of the neutralized specie. These absolute cross sections are necessary for calculations of the rate constants for modeling of radiative energy loss in electron beam heated plasma phenomena. They are also relevant to the understanding of alkali resonance line emissions originating in the ionospheric night glow. Second, in the course of determining the absolute cross sections, the polarization ratios of the atomic emissions are also measured. It is thought that these polarization measurements will provide a sensitive probe of the relative spatial orientation of the collision partners in the quasi-molecule-ion intermediate complex. In addition, polarized emission arising from a non-random population of degenerate atomic orbitals can be used to construct bond overlap models of the quasi-molecular intermediate, and thus some insight can be obtained into the preferred collision geometries. Third, the appearance of structure in the emission cross sections can be used to study the possible occurrence of quantum interferences between charge transfer and other energy processes.

The essential thing is that these studies can yield detailed information on the molecular nature of the collision complex, in spite of the relatively high ion beam energy used in these experiments. Finally, the functional dependence of the radiat ive charge transfer process is analyzed in terms of the collision energy, the principal quantum numbers of the active electron, and the endoergicity or energy defect of the overall process.

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**Cover Caption**

*Spherical particles enlarged 3,500 diameters are shown in this scanning electron micrograph. Smooth rubbing-wear particles are seen behind the larger sphere.*

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