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STRESS-CORROSION FAILURE

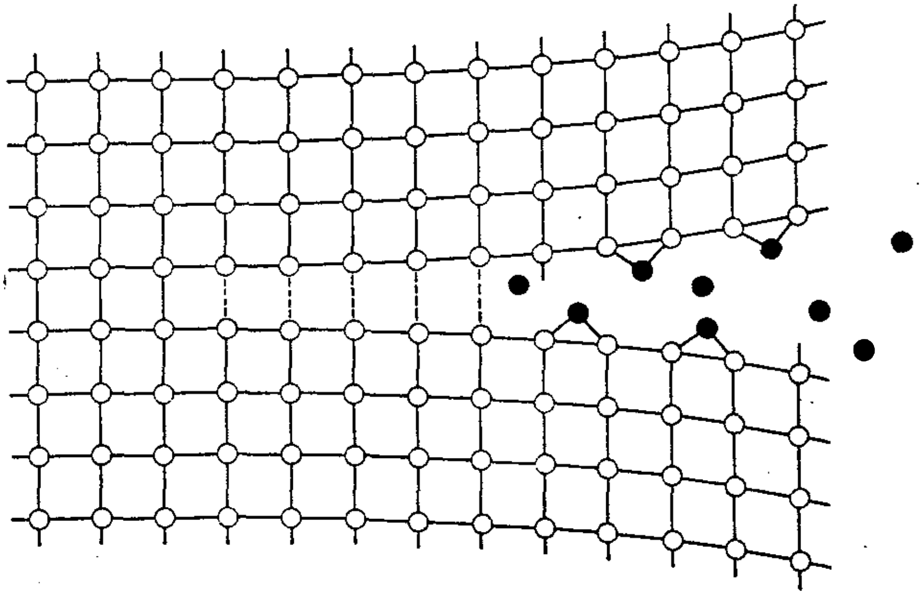
In some chemical environments alloys give way under stresses it was assumed they could bear. The importance of this phenomenon increases with the growing diversity of circumstances in which alloys are used

by Peter R. Swann

Men have come to stake their lives in many ways on the strength and reliability of metals. Occasionally, to our dismay, metal structures give way under stresses they were assumed to be able to bear. These sudden breakdowns can generally be traced to one of three causes: fatigue, which results from the repeated application of a relatively small stress; creep, a slow deformation that usually occurs at higher temperatures, and stress-corrosion failure, a weakness peculiar to alloys in some chemical environments. There are other types of failure caused by the incompatibility of a metal and its environment, but stress-corrosion failure is the most widespread and significant.

Incidents of stress-corrosion failure were first recorded in the 19th century by jewelers who observed that their cheaper gold alloys became brittle when exposed to certain solutions containing chloride ions. At the beginning of this century the phenomenon received wider notice when the brass cases of cartridges issued to the British army developed curious cracks on their arrival in India. Because the tendency to crack was greatest during the rainy season, the weakness was first known as "season" cracking. It was eventually shown that the cracking was caused by the combined action of traces of ammonia in the moist atmosphere and stresses remaining in the cartridge cases from the time of fabrication. If either the ammonia or the residual stresses were removed, the tendency to crack was eliminated. Once it was established that stress and a corrosive environment must act together to induce cracking, the more descriptive term "stress-corrosion" cracking was adopted. It is now known that stress-corrosion affects many alloys and has caused the explosion of boilers, the failure of aircraft parts and metal implants in the human body and costly breakdowns in nuclear reactors and chemical and manufacturing plants. The phenomenon is not restricted to metals; it occurs in plastics exposed under stress to some organic chemicals, and also in glasses subjected to stress in the presence of steam.

How does the environment of an alloy initiate a fracture and enable it to propagate even under a small stress? To this basic question can be added many others. Why are metals of high purity immune to stress-corrosion cracking? (In some cases only a few hundredths of 1 percent of impurity is required to make a metal susceptible.) Why do some environmental conditions cause cracking in one alloy and not in others? (Brasses, for example, fail when subjected to stress in the presence of ammonia, but copper-gold alloys do not.) Is the role played by corrosion essential to the failure? In many instances the degree of chemical attack from the environment is small, and sometimes no evidence of corrosion is visible to the unaided eye. Research into these questions has called for the application both of physical metallurgy (the study of mechanical properties such as strength and ductility) and electrochemistry (the relation of chemical changes to the flow of electricity). Ultimately both disciplines are concerned with the nature of events taking place on the atomic scale.



ATOMS AT TIP OF CRACK in a crystalline solid are represented schematically. One theory of stress-corrosion failure holds that certain ions from atmosphere (*black*) can penetrate to atoms at tip of crack and become strongly adsorbed, thus lowering the binding energy between these atoms and enabling the crack to propagate at an unusually low stress.

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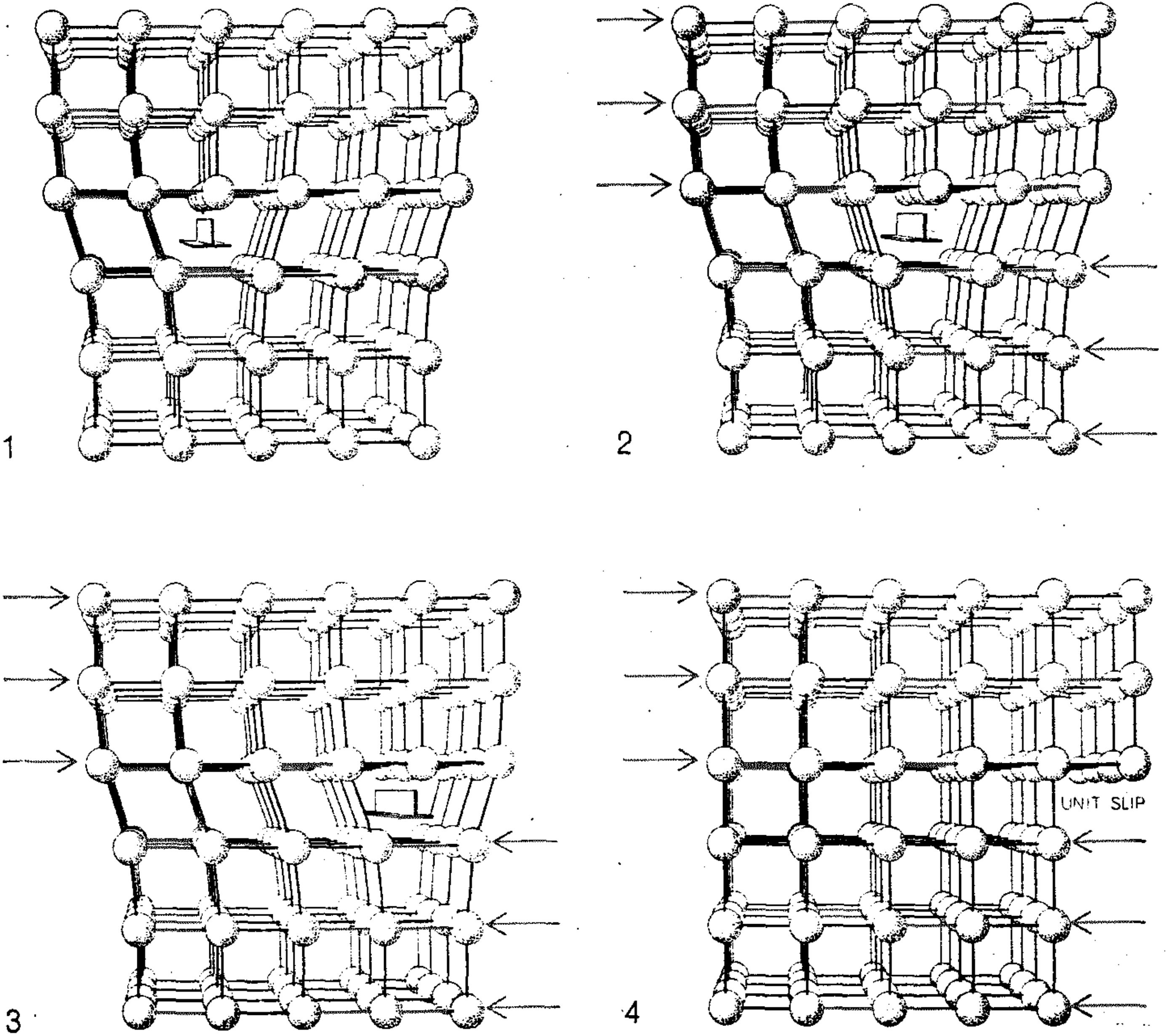
Although it is not usually obvious from their external shape, solid metals are crystalline; that is, their atoms are arranged in a regular three-dimensional array. In order to visualize how a crystalline structure would fracture we must consider the arrangements of atoms that would prevail at the tip, or leading edge, of a crack [*see illustration on preceding page*]. The atoms at the surface of the crystalline structure are not bonded on all sides, and consequently their energy is greater than the energy of the atoms inside the structure. This excess energy is termed surface energy. The atoms at the tip of the crack, which are displaced by the stress from their normal position, are in an intermediate energy state. Their excess energy is called elastic energy, and it can be increased to the level of surface energy by increasing the stress. A further increase in elastic energy will cause these atoms to move into positions characteristic of surface atoms and will allow the crack to advance a distance equivalent to the diameter of a few atoms.

The magnitude of the surface energy can be measured, and from it the value of the stress required to propagate the fracture can be calculated. This simplified method of determining the stress required for the propagation of a crack provides a somewhat low estimate because it does not take into account the fact that metals commonly undergo some plastic deformation before fracture. But even if we use the underestimated capacities of metals determined by this method, we find that stress-corrosion failure of an alloy ordinarily occurs at stresses of less than a hundredth of the load the alloy is assumed to be capable of sustaining.

How can fracture occur at so small a stress? One view is that the chemical environment has a considerable influence on the surface energy of the susceptible alloy. It is believed that cer-

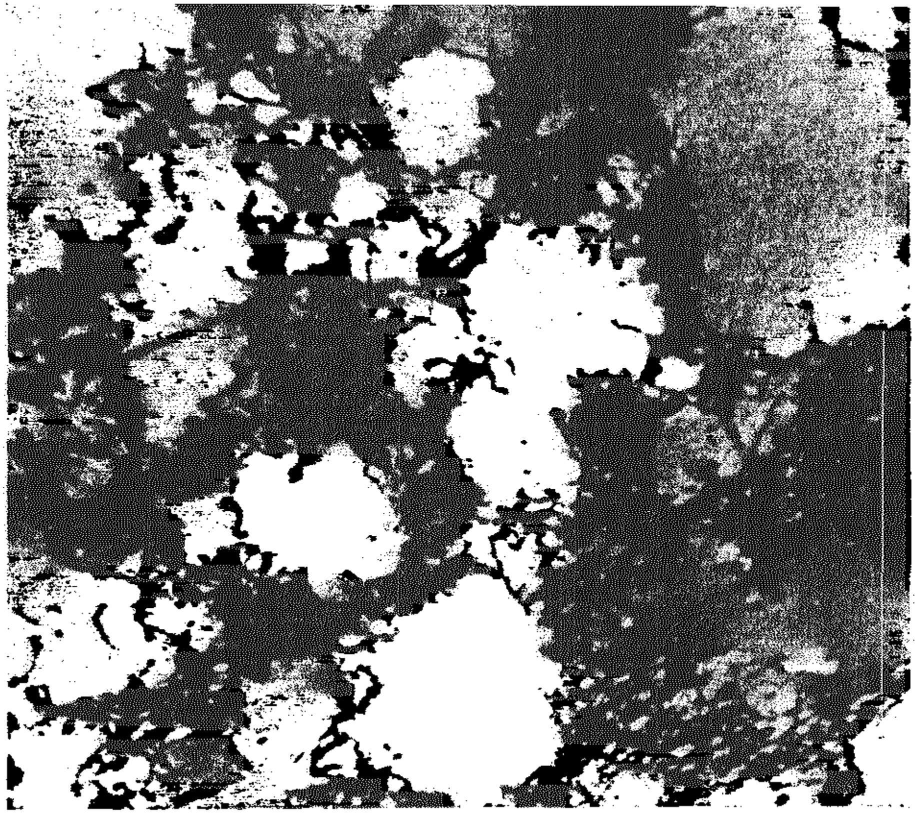


DISLOCATION is a defect involved in the stress-corrosion cracking of alloys. The edge dislocation, represented by the inverted *T*-shaped symbol, occurs where a plane of atoms is absent from the crystal lattice (*panel at top left*). When a small shearing force is applied, a simple flip in atomic bonding makes the dislocation jump one cell to the right (*top right*). Ultimately the dislocation reaches the edge of the crystal, producing a unit slip, or slip step. Plastic deformation of the metal involves many such slip steps in sequence.

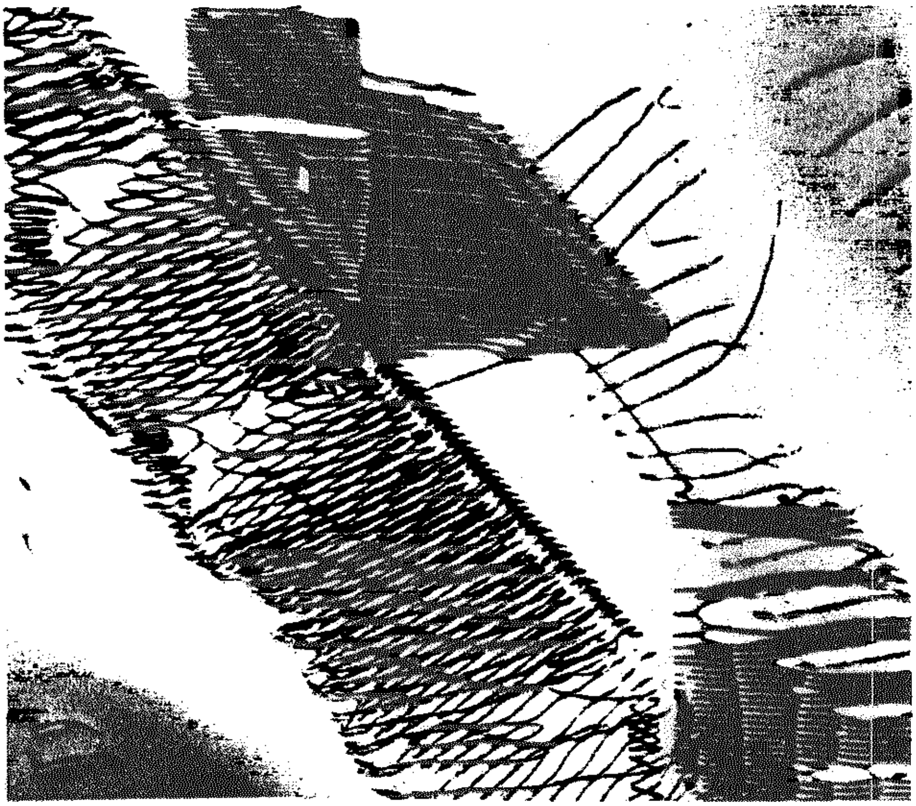
tain ions in the environment can diffuse to the tip of the crack and be adsorbed there and on the nearby walls. The adsorbed ions would lower the binding energy between surface atoms to the extent that crack propagation could occur at small stresses with little plastic deformation. This theory would explain the specific effectiveness of stress-corrosion environments. For any particular alloy only a few ions ordinarily present in the environment would be sufficiently small to diffuse to the tip of the crack (the radius of which would be on the order of the distance between the atoms of the alloy) and would also be capable of being adsorbed to the surface of the alloy. The theory holds up when it is applied to the environmentally induced fracture of nonmetals and to the cracking of pure metals and alloys in the presence of liquid metals. It does not explain, however, the very slow rates of stress-corrosion cracking in water solutions and the absence of such failure in pure metals.

A competing theory of stress-corrosion cracking proposes that fracture begins and proceeds with the electrochemical dissolution of the alloy along particularly reactive paths to form pits that eventually deepen into tunnels. The development of many corrosion tunnels would weaken the alloy so that a crack could be propagated by a small stress. One of the main premises of this theory is the existence of paths of enhanced reactivity throughout the susceptible alloy. After stress-corrosion failure occurs the path of a crack can be examined; often we find that the crack has followed the boundary between the adjoining grains, or small single crystals, that make up the metal. This intergranular fracture is readily explained. The distribution of elements in an alloy is not homogeneous, and the composition at or near a given grain boundary is different from the average composition of the alloy as a whole. Accordingly the chemical reactivity of the grain-boundary region is high.

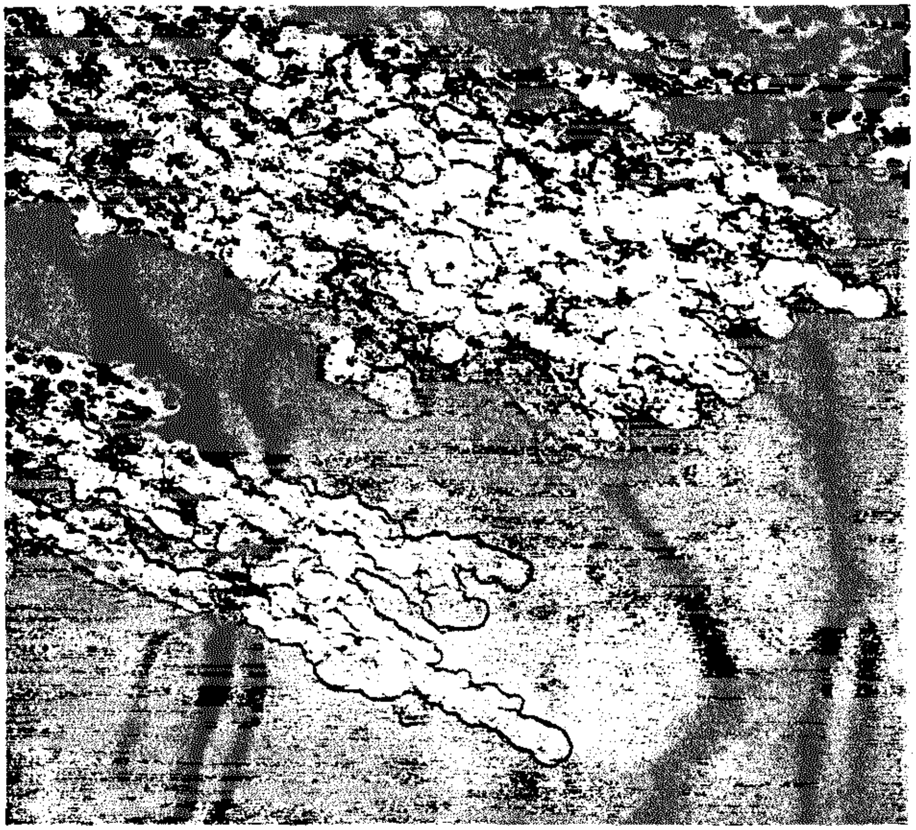
In many alloys that are susceptible to stress-corrosion failure, however, the fracture path shows no preference for grain boundaries at all. In fact, stress-corrosion cracks can be produced in large single crystals of the susceptible alloys. This type of fracture, called transgranular fracture, is not so readily explained. Why do cracks propagate across the grains in some alloys? In an attempt to discover the nature of the transgranular paths the author, working under J. Nutting at the University of



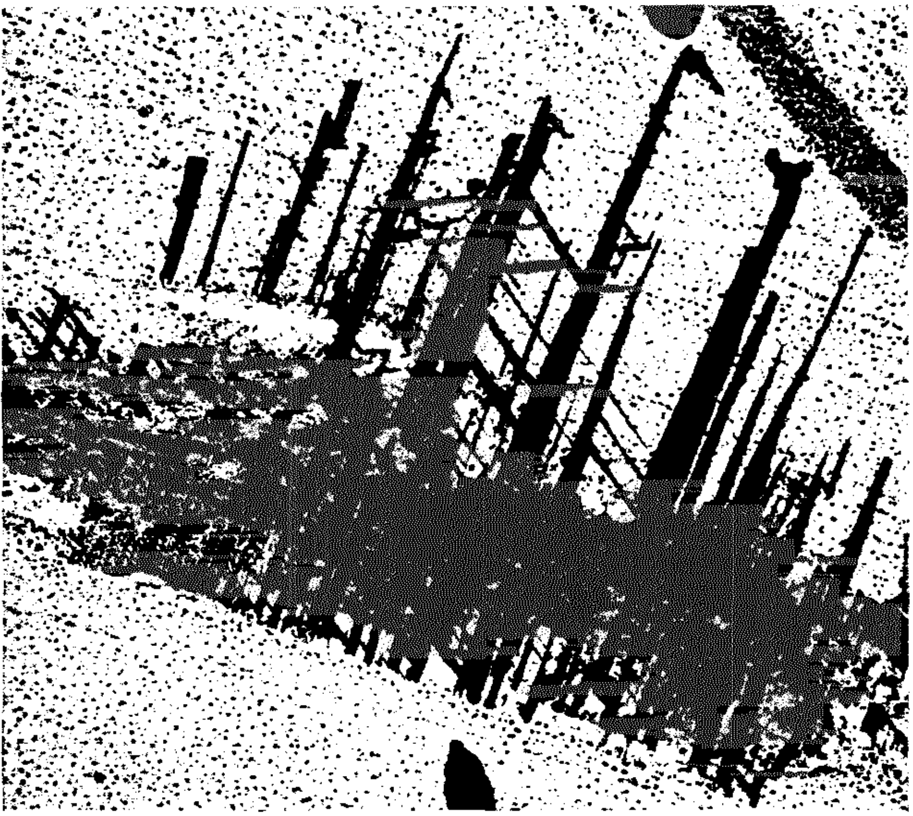
DISLOCATION "TANGLES" produced by deforming a specimen of pure copper are enlarged some 22,000 diameters in this electron micrograph. The image of an individual dislocation is some 50 atoms in width; in the micrograph each dislocation appears as a short dark line. The distribution of tangled dislocations is typical of pure metals and dilute alloys.



PLANE ARRAYS OF DISLOCATIONS is characteristic of their distribution in many concentrated alloys. This electron micrograph enlarges some 20,000 diameters the dislocations left after deformation of a concentrated copper alloy. The pattern suggests that during deformation groups of dislocations move one behind the other on well-defined planes.



CORROSION TUNNELS develop from pits on the surface of an alloy that elongate in the direction of closest atomic packing (*toward bottom right in this case*). Tunnels are some 250 atoms in diameter; this micrograph of an alloy enlarges them some 100,000 diameters.



LININGS OF TUNNELS, the needle-like objects in this micrograph, were made to cling to an oxide replica of a stainless-steel surface while the alloy in which they had formed was selectively dissolved. The micrograph was made by N. A. Nielsen at the Experimental Station of E. I. du Pont de Nemours and Company in Wilmington, Del. It indicates that corrosion tunnels are nucleated (that is, they form initially) in rows on the surface of the alloy.

Cambridge and later with Howard Pickering and David Embury at the Edgar C. Bain Laboratory for Fundamental Research of the United States Steel Corporation in Monroeville, Pa., employed the technique of transmission electron microscopy to examine susceptible alloys at magnifications large enough to resolve most crystal defects.

This technique involves reducing the specimen to a thickness of about 500 atoms. Electrons accelerated to high velocities can then be caused to penetrate the specimen and make visible the defects in the crystal lattice. The kind of defect of immediate interest to us is called a dislocation. Such a defect is created when one part of a crystal is displaced with respect to the rest [*see illustration on page 74*]. The boundary of the region that slips—the dislocation line—can be made to move over a crystal plane (called a slip plane) by the action of an external stress. The growth of the slipped region is complete when the dislocation line passes through the crystal surface to form a step. It is the motion of dislocations that allows a metal to be deformed in a ductile manner, but since the slip associated with each dislocation is only of atomic dimensions, the motion of billions of dislocations per cubic inch of metal is needed to produce even a slight plastic deformation. Fortunately for investigators of metals a dislocation is visible in a micrograph made with the electron microscope because the distorted crystal lattice near the axis of the dislocation diffracts the illuminating electron beam more strongly than the undistorted crystal that surrounds it. The dislocation thus appears as a thin dark line.

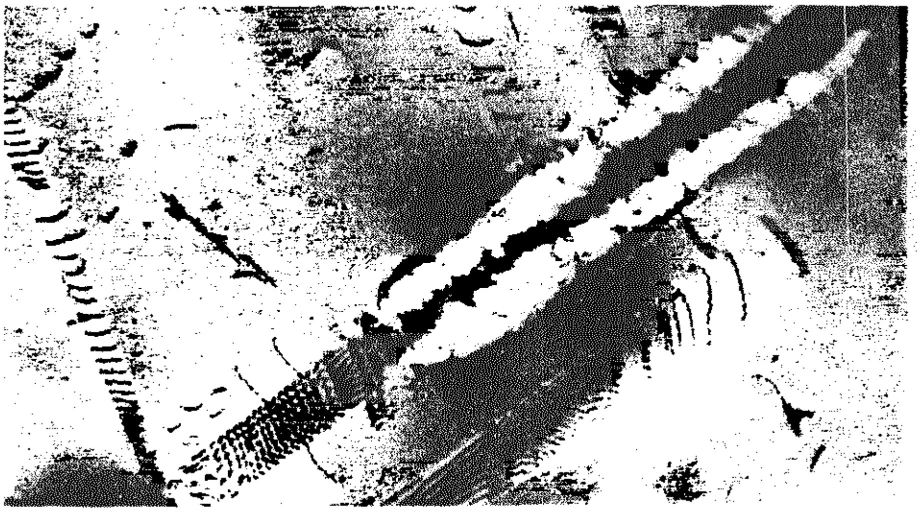
Our initial experiments compared the structure of deformed copper alloys of different composition. Specifically we sought to determine why dilute alloys—that is, alloys containing relatively little of the alloying element or elements—do not show transgranular cracks when they fail by stress-corrosion, whereas the more concentrated alloys do. In some of the electron micrographs we made we observed a striking effect of the concentration of the alloying element (or elements) on the distribution of dislocations in copper alloys. At a low concentration the dislocations form tangles with a cellular configuration; at a concentration high enough for transgranular stress-corrosion cracks to occur the dislocations move one behind the other in groups on well-defined planes [*see bottom illustration on preceding page*]. Apparently transgranular cracks are formed only when the deformation takes place in this way.

The correlation of groups of dislocations in planes and the formation of transgranular cracks has been found to apply to many alloys susceptible to stress-corrosion failure. One such alloy of iron, which contains chromium, nickel and small but important amounts of nitrogen and carbon, is a stainless steel with a useful property: its crystal structure changes when the alloy is cooled to the temperature of liquid air. The room-temperature form, called austenite, is susceptible to transgranular cracking in a solution of boiling saturated magnesium chloride, but the low-temperature form, called martensite, does not fail in the presence of this solution. By slowly lowering the temperature we can obtain a specimen of this stainless steel that is partially transformed from austenite to martensite; thus we can directly compare the distribution of dislocations in the austenite and martensite structures. The dislocations of the martensite structure do not form in planes, but dislocations in the austenite structure do. Since no local changes in chemical composition can occur during the low-temperature transformation from austenite to martensite, it is clear that susceptibility to stress-corrosion cracking depends on some physical characteristic of the susceptible alloy.

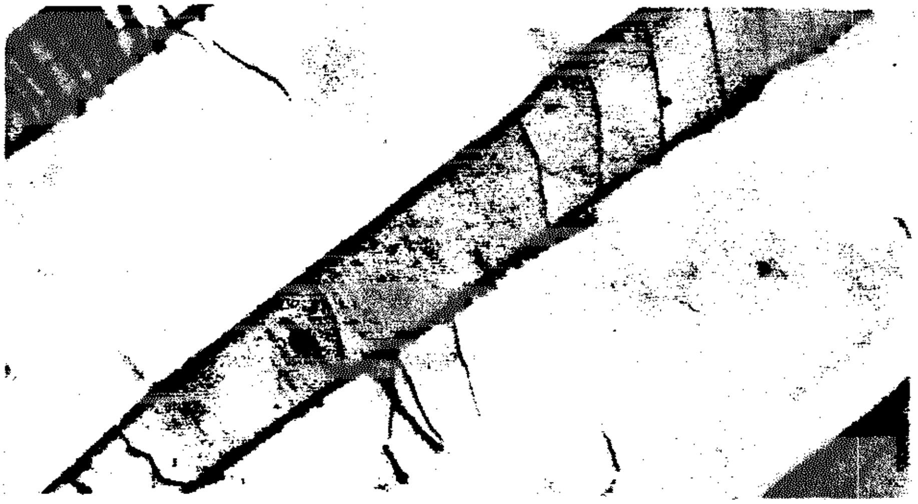
These early experiments led us to suppose that the plane groups of dislocations might themselves provide the reactive path in cases of transgranular cracking. To test this idea we exposed specimens of various alloys to stress in corrosive environments, so that we could observe with the electron microscope the first stage of chemical attack. To our disappointment the plane groups of dislocations were not attacked preferentially; instead attack occurred randomly over the surface of the susceptible alloys, taking the form of pits that ranged from 20 to 500 atoms in diameter. The pits continued to grow in the direction of the most closely spaced atoms of the crystal structure, elongating into tunnels. The rate at which the tunnels developed was quite high: it was comparable to the known rate at which cracks propagate during stress-corrosion failure.

Corrosion tunnels have also been revealed in electron micrographs made by N. A. Nielsen of the Experimental Station of E. I. du Pont de Nemours and Company in Wilmington, Del. Nielsen

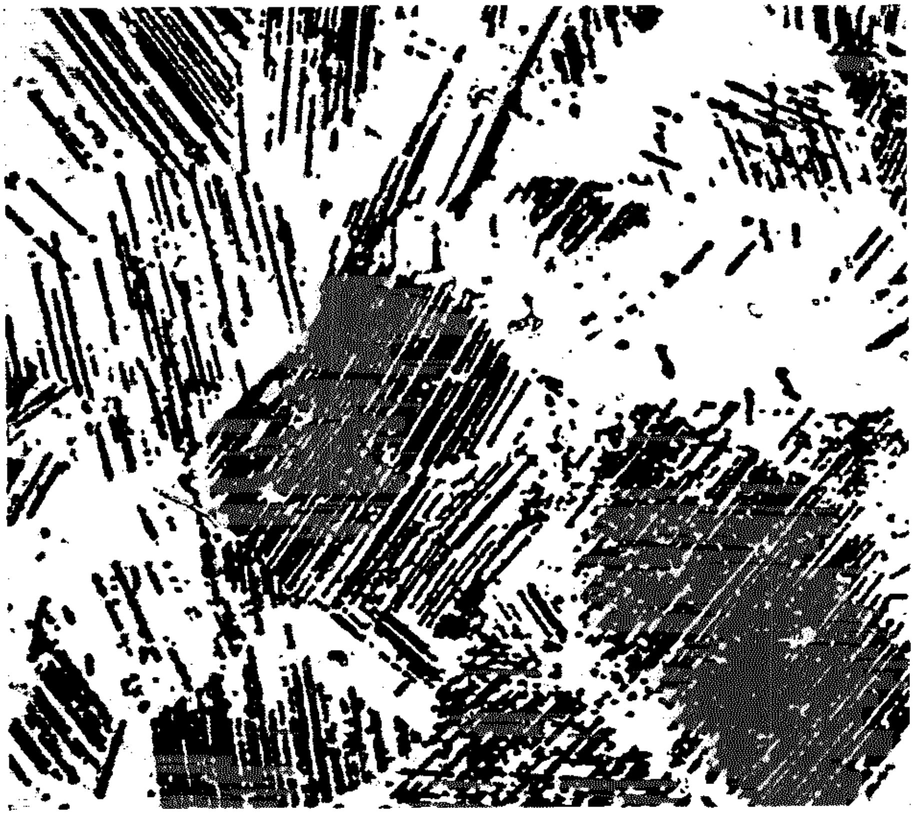
EARLY EFFECT OF CORROSION, the formation of pits (rows *of black dots*), is shown directly on the surface of a stainless steel. The dislocations (*black lines*) create slip steps that serve as nuclei for pits. The slip steps themselves cannot be seen in this micrograph.



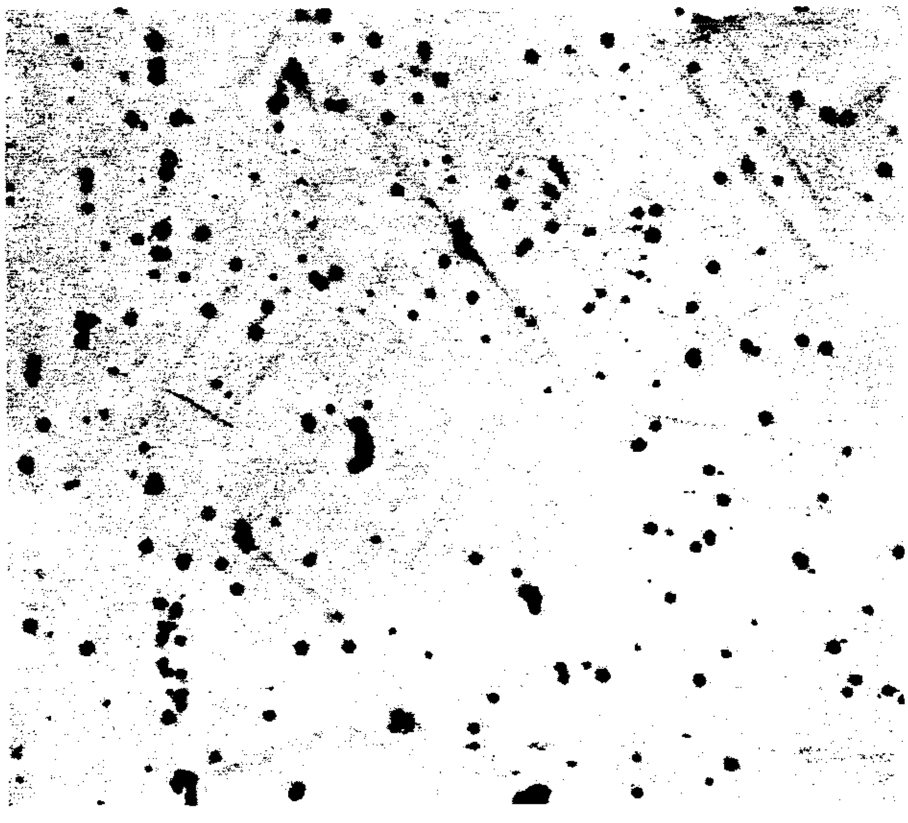
FINAL EFFECT OF CORROSION on a thin specimen of alloy is a slot that pierces it. Corrosion slots are formed by tunnels merging; two appear in this micrograph (*white regions*).



SLIP TRACES, the paths made by movement of dislocations, appear as long dark lines and dislocations as short vertical lines in this micrograph. A stressed alloy was immersed in a solution that liberated tiny particles of platinum (*black dots*) when it decomposed. The presence of these particles near the slip traces indicates an area of enhanced reactivity.



UNPROTECTED SURFACE of a freshly deformed stainless-steel specimen was exposed to *a solution that decomposed* so as to liberate platinum particles at the chemically active slip steps (*straight dark lines*). Slip steps in any grain of the alloy are approximately parallel.

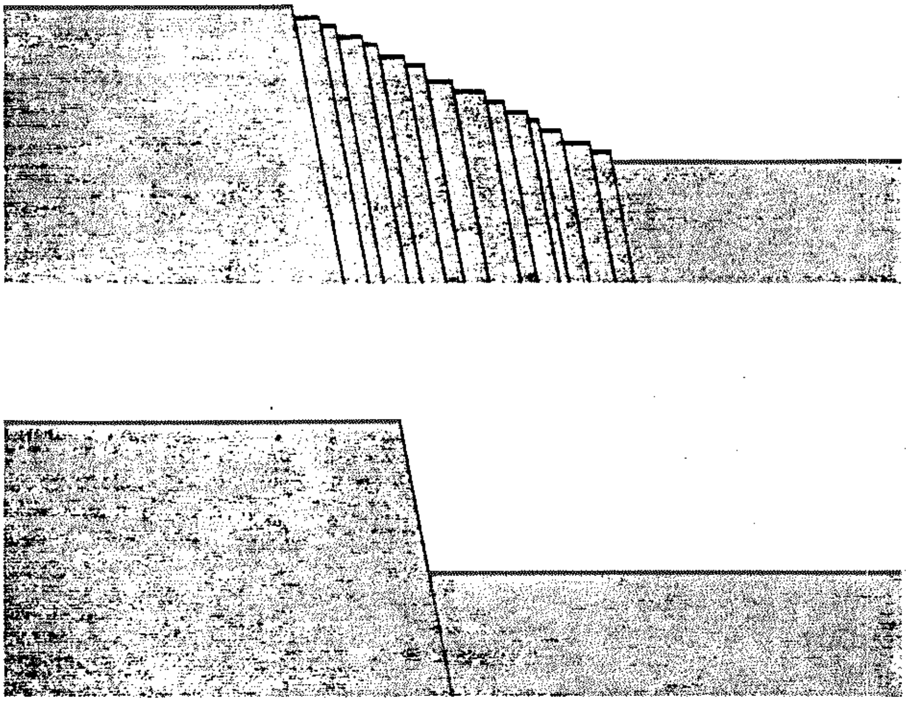


PROTECTED SURFACE of a stainless-steel specimen that had been deformed before it was immersed and stressed in a solution known to cause stress-corrosion failure was also exposed to a solution that liberated platinum particles. These deposited in a random way rather than near the slip steps. It appears that only newly formed slip steps are chemically reactive.

developed a technique for examining stress-corrosion cracks in stainless steels that involves oxidizing the surface of the corroded specimen and then dissolving the underlying metal. This procedure leaves an oxide replica of the surface, approximately 200 atoms thick, to which any corrosion products would adhere. The linings of the tunnels are of course corrosion products, and so Nielsen was able to isolate them and make micrographs of them. They appeared as long, hollow threads sticking out of the oxide replica [*see bottom illustration on page 76*]. The tunnels themselves were judged to have formed initially on some defect in the crystal structure, and the direction of their growth seemed to be related to the crystal lattice of the alloy. Nielsen's pictures also showed for the first time a definite link between the corrosion tunnels and the stress-corrosion crack itself. In one of his micrographs a network of corrosion tunnels can be seen in front of a region in which the tunnels had grown together to form a transgranular crack.

The precise nature of the defects that provide nuclei, or points of formation, for the corrosion tunnels cannot be determined from oxide replicas of the alloy surface. This can best be done by experimenting with thin films of the alloy itself. In our laboratory we have stressed alloy specimens for a few seconds in a boiling saturated solution of magnesium chloride and then examined them in the electron microscope for signs of chemical attack. At the earliest stage of nonrandom attack discernible to us the nuclei of corrosion tunnels appear as horizontal rows of black dots. It is important to note that the nuclei of the corrosion tunnels are not provided by the dislocation lines themselves but by the slip steps they have created on the top and bottom surfaces of the thin specimen. Several examples of corrosion pits more than 100 atoms deep were observed along slip steps after only a few seconds of exposure to the stress-corrosion environment. One micrograph we obtained illustrates the final stage of crack formation, in which the pits have grown together and completely penetrated the thin specimen. This micrograph helped to dispel our notion that the tunnel is nucleated at the plane groups of dislocations; clearly nucleation occurs at the traces of slip planes on the surface.

The sites where the dissolution of the alloy actually begins can best be revealed by a technique of platinum "decbration" that was originally used by Nielsen in conjunction with his surface-replica technique. This method exploits the fact that ions of chloroplatinic acid will decompose on the surface of an alloy adjacent to regions in which the metal is being dissolved. The tiny particles of platinum liberated when this decomposition occurs can be detected in the electron microscope because they strongly scatter the electrons in the illuminating beam. When the platinum-decoration technique is applied to stressed thin specimens, the chemical activity of the slip steps is demonstrated plainly. One can thus observe in the same electron micrograph slip traces (paths made by the movement of dislocations in thin alloy specimens), the dislocations that produced them and the particles along the slip step [*see bottom illustration on page 77*].



PROTECTIVE FILM on the surface of an alloy such as a stainless steel can be broken in one of two ways, depending on the distribution of the shear (that is, the type of slip). Fine slip (*top*) exposes a much smaller area of underlying metal than coarse slip (*bottom*).

Our proposal that slip steps provide nuclei for stress-corrosion cracks was apparently in conflict with the experimental observation that the density of surface slip steps is often 100 to 1,000 times greater than the density of stress-corrosion cracks. This discrepancy was explained, however, by another experiment involving stainless steels. Stainless steels would be very reactive alloys if it were not for a thin surface film, chemically inert to most environments, that forms when such steels are exposed to air. This film prevents further corrosion and gives the steels their stainless qualities. It seems safe to assume, in working with stainless steels, that the traces along which corrosion tunnels form are precisely those sites where the protective film has been broken by the formation of slip steps.

Two stainless-steel specimens were electropolished to give them similar surfaces and then were deformed under stress to produce surface slip steps. The first specimen was immersed for one minute in a boiling saturated solution of magnesium chloride that had been "doped" with chloroplatinic acid to help reveal the chemically active sites on the surface of the specimen. Using a light microscope, we observed the expected result: crystals of platinum deposited along the surface slip steps in the various grains of the alloy [*see top illustration on opposite page*]. The second specimen was immersed in an undoped magnesium chloride solution for one minute, after which it was transferred to the doped solution for another one-minute immersion. We observed that the prior immersion in undoped magnesium chloride solution eliminated the enhanced reactivity of the slip steps; they ceased to be preferred sites of platinum decoration [*see bottom illustration on opposite page*]. We concluded from this experiment that the damage to the surface film resulting from the slip steps produced by deformation is rapidly repaired during exposure to the boiling magnesium chloride solution. Whether dissolution can continue once nucleation takes place must depend on the rate of film repair compared with the rate of film breakdown caused by the motion of dislocations. Consequently it appears that only slip steps that are created during exposure to the cracking solution have the potential of nucleating and propagating stress-corrosion cracks.

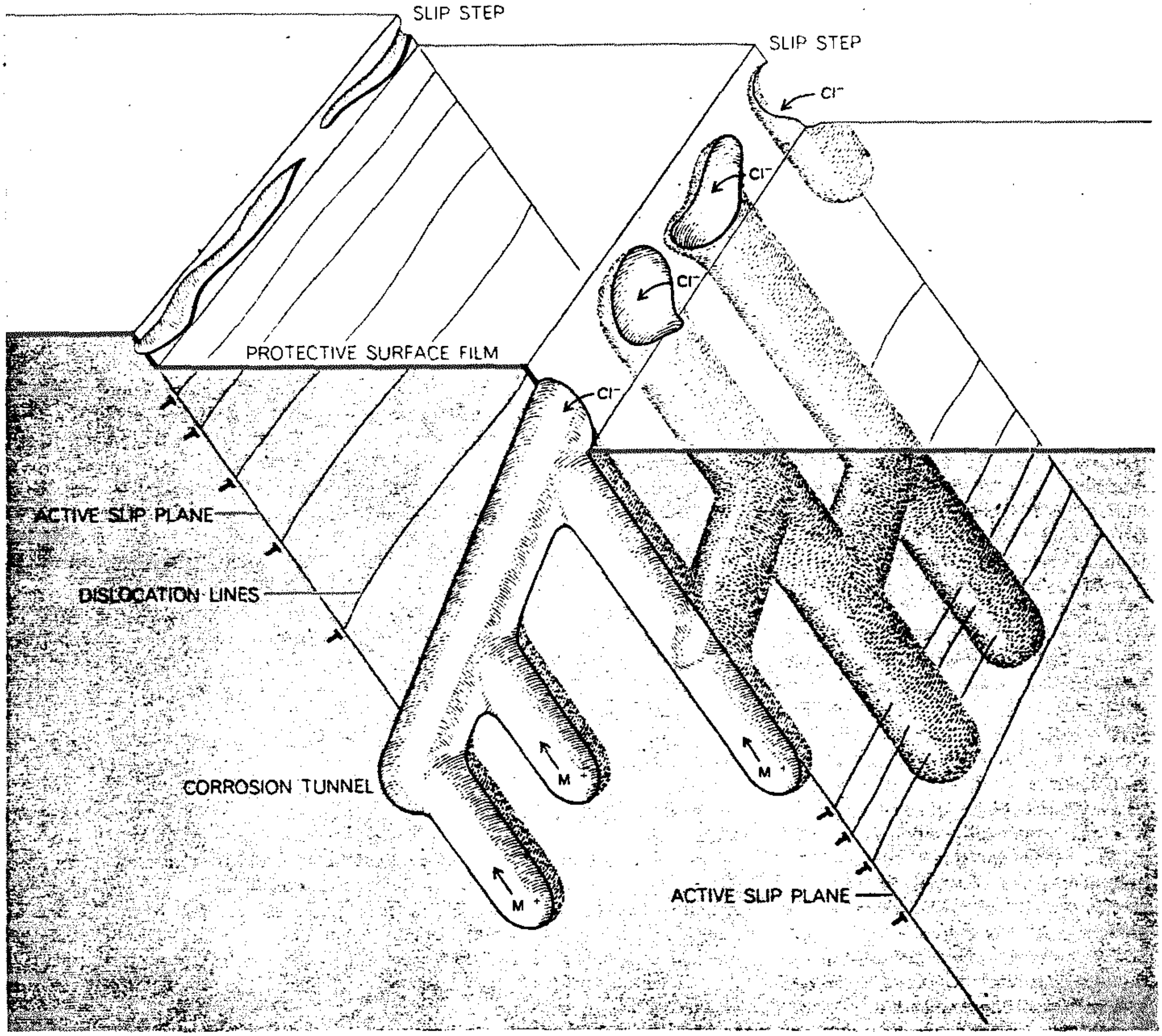
It is to be expected that the amount of damage suffered by the protective surface film is determined not only by the amount of slip but also by its distribution. The same amount of slip will expose a greater area of unprotected surface when all of it occurs on one plane (this is called coarse slip) than when it is distributed in small amounts over several planes (fine slip). It is more likely that the surface film would be broken in alloys forming coarse slip steps. This helps to explain the connection between the distribution of dislocations and the mode of stress-corrosion cracking: those alloys that form plane groups of dislocations also form coarse surface slip steps.

The validity of this argument can be demonstrated by a simple experiment involving a stainless steel that can take the form of martensite and austenite. First the steel is refrigerated to form a martensite structure and deformed to produce fine slip steps. Then it is exposed to the platinum-doped solution for a few minutes and examined in a light microscope. The fine steps are not revealed by platinum decoration (the chemical attack is randomly nucleated), indicating that this structure is resistant to stress-corrosion cracking. When the austenite version of the alloy is treated in the same way, however, it is deformed by producing coarse slip steps that *are* chemically active, and this structure is susceptible to transgranular cracking.

So far we have been concerned mainly with the nature of the nucleation site that leads to transgranular stress-corrosion failure. The equally important mechanism by which the corrosion tunnel forms at an active slip step is at present poorly understood. It is clear, however, that when the protective film on the surface of stainless steel is ruptured by the formation of a slip step, atoms of the alloy must come directly in contact with the corrosive environment and can enter into solution to become positively charged ions. The extent of this reaction is determined by the relative rates of corrosion and repair of the protective film. The formation of a locally high concentration of positive metal ions is expected to attract to the slip step chloride ions and other negatively charged ions in solution. In the case of stainless steels it is known that chloride ions (and other ions of the halogen family) cause a breakdown of the protective film. We also know that the solubility of the elements that compose the steel—iron, nickel and chromium—is unusually high in the presence of a strong concentration of chloride. The enrichment of chlorides in the region of a slip step therefore favors continued localized corrosion.

Another factor must be considered, however. The electric potential developed at the initial corrosion sites tends to retard the dissolution of metal in nearby areas, and it is thought that corrosion pits interfere with one another's growth if they are too closely spaced. This factor also tends to prevent individual pits from increasing in diameter, and since the planes of a crystal in which atoms are most closely packed are the slowest to dissolve, the walls of the pits will tend to become parallel to these planes. These considerations might explain why a given corrosion pit will grow in the direction in which atoms are most closely packed.

The aim of any investigation into the cause of a certain weakness is to discover a means of overcoming it. The results presented in this article indicate several possible ways in which we can hope to prevent stress-corrosion cracking. The process begins with the physical rupture of the thin, protective surface film; secondly, the metal atoms at the slip step enter the stress-corrosion-cracking environment as the protective film starts to cover the newly exposed



STEPS THAT LEAD TO CRACKING of a stainless steel are depicted. Under the action of an applied stress, dislocations move to the surface, forming slip steps that fracture the protective film and expose metal ions (*represented as* M^+) to the corrosive environment. Chloride ions (Cl^-) concentrate at a slip and retard re-formation of the protective film; this enables corrosion pits to elongate and ultimately form tunnels. The continued motion of *dislocations on the slip plane* prevents these corrosion tunnels from becoming inactive. They grow sideways, merging in the final stage of the stress-corrosion process (not depicted) to form a crack.

metal surface; thirdly, specific ions that hinder the formation of the protective film are attracted to the slip step and corrosion tunnels become nucleated; lastly, the motion of dislocations under the action of the applied stress ensures the continued growth of the corrosion pits. The prevention of any one of these important steps in the formation of a crack should eliminate susceptibility to transgranular stress-corrosion cracking.

One obvious approach is to try to reduce the damage to the protective film by using various metallurgical techniques that discourage dislocations from gliding in large groups on single planes. This approach has met with some success in the laboratory, but more must be done to develop a commercial alloy.

Another approach is to try to prevent the dissolution of metal at the slip steps. This can be achieved most easily by establishing an electric circuit in which the current flows in a direction opposite to the small currents generated during the dissolution of metal. An alternative method of reducing localized corrosion would be to hasten the repair of the protective film. In some cases this can be achieved by adding certain chemicals to the stress-corrosion environment. With both of these approaches it has been shown in the laboratory that the stress-corrosion cracking of stainless steels can be prevented under some environmental conditions.

Given the variety of industrial uses of alloys, it is often not possible to control closely the environment in which a given metal will be placed. The most desirable methods for preventing stress-corrosion failure should therefore involve some minor modification of the alloy itself. We could, for example, add small amounts of alloying elements that form insoluble compounds with the stress-corrosion environment. The precipitate formed during corrosion might then hinder the growth of corrosion tunnels and enable the protective film to re-form over the slip step.

In conclusion it should be mentioned that although we have dwelt mainly on the problem of the transgranular stress-corrosion failure of stainless steels, parallel experiments in our laboratory and in Nutting's laboratory (which is now at the University of Leeds) suggest that the same mechanism applies to many other susceptible alloys. There are also indications that the mechanisms of intergranular and transgranular stress-corrosion cracking are basically the same, in which case the applicability of our findings would be widened.