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The Effects of Machining and Grinding on the Stress-Corrosion Cracking Susceptibility of Metals and Alloys

by

Dr. Harold W. Paxton
Head, Department of Metallurgy and Materials Science

and

Dr. R. P. M. Procter
Department of Metallurgy and Materials Science
Carnegie - Mellon University

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I Introduction

I. 1. Current Importance of Stress-Corrosion.

In a written discussion of a paper on the stress-corrosion of austenitic stainless steels published in the Transactions of the American Society for Metals in 1940 (1), the opinion was put forward that "... It would not seem, therefore, that we may anticipate failures of this type occurring in unsuspected places, so the industrial implications of this phenomenon do not loom large. Failures are rare and will become more so as understanding spreads." In spite of this optimistic prediction, it can be stated with some confidence that the reverse is true today; two examples should suffice to emphasize this point. Firstly, stress-corrosion cracking resulted in the scrapping of a whole class of submarines belonging to a NATO member country a few years ago. Secondly, and more recently, the titanium alloy to be used as the primary structural material in the Supersonic Transport (S.S.T.) was changed, after a great deal of development work had been carried out, from Ti-8Al-1Mo-1V, which has very poor stress-corrosion resistance, to Ti-6Al-4V, which is considerably less susceptible. Nevertheless, it may well be that actual service failures attributable to stress-corrosion will become less common as an awareness of the dangers of the phenomenon spreads. It is therefore urgent and important that practicing engineers of all disciplines should be concerned about these dangers, and also that they should be aware of the techniques that are available for minimizing them.

1.2. Outline of Paper.

This paper will be divided into three sections. Firstly, a very brief summary of the phenomenology of stress-corrosion cracking will be presented. Next the metallurgical and other changes which are brought about in a metal surface by machining and grinding operations, and which may have an important bearing on the stress-corrosion susceptibility of a particular alloy, will be considered. Finally, by means of a literature survey, an attempt will be made to relate these two sections to experimentally-observed data, and hence to produce some general recommendations.

II Stress-Corrosion Cracking

II. 1. Definition of Stress-Corrosion.

Any general and generally acceptable definition of stress-corrosion is extremely difficult to formulate. However, the statement that the phenomenon of stress-corrosion cracking results in a degradation of the mechanical properties of a material, under the joint action of stress and a corrosive environment, which is greater than can be accounted for by the sum of the separate effects of the stress and the environment alone, is reasonably satisfactory. It should be noted at once that the stress must

be tensile or have a tensile component (stress-corrosion cracking has never been observed with compressive stresses) but that the stress may be either residual or applied. The environment in virtually all cases is only very midly corrosive as far as evidence of "general corrosion", in the absence of stress, is concerned.

II. 2. Historical Background.

Around 1900 in India, brass cartridge-cases of the British Army suffered "season-cracking" when stored close to stables during the summer. This cracking, which was quickly diagnosed as being due to a combination of residual stresses and the hot, damp, ammoniacal atmospheres, is the first recorded service failure which was recognized as being due to stress-corrosion (2). Roberts-Austen, however, had observed the phenomenon in Au-Cu-Ag alloys in the laboratory some 15 years previously (3).

II. 3. Materials Showing Stress-Corrosion.

Since that time, stress-corrosion cracking has been very widely observed, notably in the following classes of materials:

(1) aluminum alloys, (chloride ions) (4).
(2) magnesium alloys (5).
(3) copper-base alloys (6), (ammonia and ammonium ions).
(4) high-nickel alloys (7).
(5) titanium alloys (8), (chloride ions and fused chlorides).
(6) mild steels (nitrates and hydroxides) (9).
(7) stainless steels (chloride ions) (10).
(8) high-strength alloy steels (11).
(9) miscellaneous other metals and alloys (lead (12), beryllium (13), zirconium (14) and silver and gold-base alloys (6)).

Thus, although stress-corrosion cracking has been reported in all the common alloy systems, it is not confined to metals. Phenomenologically similar failures are observed in ceramics and glasses (static-fatigue) (15), polymeric materials (stress-crazing) (16) and in some inorganic crystals (17). Until recently it had been generally accepted that pure metals were immune to stress-corrosion but evidence is being accumulated to show that this may not be so (18, 19 inter alia); however, there is no doubt that pure metals (99.99% or better) have a far greater resistance to stress - corrosion cracking than do alloys or "commercially pure" metals. It is obvious from the above statements that phenomenologically similar failures are observed over a very wide spectrum of materials.

II. 4. Environments Causing Stress-Corrosion.

In many cases of stress-corrosion cracking it appears that a particular ionic or molecular species is especially effective in causing the stress-corrosion; some of the better documented examples of this effect are shown in the table above in parentheses. It should be stressed, how-

ever, that if a high-strength aluminum alloy, for example, is exposed to an environment which does not contain chloride ions, it is by no means certain that stress-corrosion cracking will not occur. Furthermore, the amount of chloride ion required to cause cracking may be minute; "hot-salt" stress-corrosion of Ti alloys, for example, was first observed at the site of a salty finger-print on a creep specimen (20). As further evidence of its ubiquity stress-corrosion of various alloys has been observed in aqueous solutions containing fluorides, chlorides, nitrates, nitrites, hydroxides, bicarbonates, ammonium ions, chromates, chlorates, sulphates, phosphates, amines, hydrogen sulphide and other radicals (7); phenomenologically similar failures are observed in distilled water, a number of organic liquids, many liquid metals (21) and, of course, widely varied gaseous environments.

II. 5. Phenomenology of Stress-Corrosion Failure.

Few, if any, structures are intentionally designed and constructed to contain cracks or microscopic crevices. Thus the course of any stress-corrosion failure can always be divided into at least two and sometimes three stages. The first stage is crack-initiation, whereby a more or less readily identifiable crack is produced in the previously "smooth" undamaged surface of the metal. The second stage is crack-propagation, when the crack grows by some "stress-corrosion" mechanism. The third stage is the ultimate failure of the service-component or test specimen. In notch insensitive materials such as brasses and stainless steels, this ultimate failure often takes the form of a leaking pipe or reaction vessel and this is a result of, rather than a stage in, the stress-corrosion failure. Even if the component does fail completely due to overloading, the fracture will be ductile. In notch-sensitive materials, however, such as high-strength steels and aluminum and titanium alloys, the stress-corrosion crack grows until the fracture-toughness of the material is exceeded, at which point catastrophic failure occurs. The ultimate fracture may be regarded as catastrophic in two senses. Firstly, the fracture is brittle, very rapid ($\sim 1/3$ speed of sound) and self-propagating; secondly, the failure is likely to involve a shattered pressure vessel, pressure hull or wing-spar. Examination of such a fracture reveals clearly the three stages of crack-initiation, slow stress-corrosion crack-propagation, and the ultimate rapid brittle-fracture. Figures 1 and 2 give practical illustrations of catastrophic and non-catastrophic failures due to stress - corrosion cracking.

II. 6. Stress-Corrosion Crack Initiation.

It is immediately obvious that, since machining and grinding operations affect predominantly the surface layers of a component and since stress-corrosion cracks generally initiate at the surface, these operations will have a predominant effect on crack-initiation and not on crack-propagation. Practical examples of stress-corrosion crack initiation will be considered in some detail in the final section. Briefly, however, the cracks

will tend to initiate at certain types of location where the net tensile stress is highest; the most important of these are:

(1) Stress-raisers intrinsic to the design of the component; rivet-holes, screw threads, sharp re-entrant corners etc.
(2) Stress-raisers extrinsic to the design of the component; areas of anomalously high residual stress resulting from poor production practice or damage in service, scratches, weld-cracks, fatigue cracks developed in service etc.
(3) Stress-raisers intrinsic to the metal or alloy; reactive grain-boundaries, active slip-steps, corrosion tunnels at planar dislocation arrays etc.
(4) Stress-raisers extrinsic to the metal or alloy; sharp, enlongated inclusions, inclusions or large precipitates which are markedly anodic with respect to the adjacent matrix, causing preferential dissolution, brittle phases formed by reaction with the environment (e.g., hydrides in Ti) etc.
(5) Crevices, depressions etc. where the corrodent can collect and/or concentrate.

Some of these sites can be eliminated or minimized by good design and production practice; others obviously can not. Even so, production and non-destructive testing techniques have not yet reached, and may never reach, the stage where it is possible to guarantee that a component contains no unsuspected flaws or incipient crack initiation sites.

II. 7. Application of Fracture Mechanics to Stress-Corrosion Testing.

The total time to failure, t_f, due to stress-corrosion, of a service component or a laboratory test specimen is the sum of the crack initiation time, t_i and the crack propagation time, t_p. The initiation time may vary from extremely short (in liquid metal embrittlement, for example, the initiation time may be negligible) to extremely long (stress-corrosion cracks will not initiate in Ti alloys in 3.5% aq. NaCl, only propagate from a pre-existing crack). Furthermore, it is clear from the preceding remarks that in any particular alloy-environment system, the initiation process is to a certain extent random and hence the initiation time often shows a wide statistical scatter.

This statistical variation in the total time to failure will clearly be less marked for notch-insensitive materials; even so, however, it presents some problems. In laboratory research and development testing, t_f is usually measured; it may be difficult to decide whether a particular alloy or heat treatment which has a longer t_f has better crack-initiation resistance or slower crack-propagation; this, in turn, makes theoretical interpretation difficult. Since a time-to-failure parameter with a wide statistical scatter is of limited use to a design engineer, mitigation of stress-corrosion cracking in notch-insensitive materials usually consists of controlling the environment where feasible, minimizing the applied and residual tensile stresses and, in extreme cases, changing from a sus-

ceptible to an immune alloy.

In notch-sensitive materials the problem was potentially more serious but in fact it has been more satisfactorily overcome quite recently by the application of the concepts of linear elastic fracture mechanics (22); this application represented a notable advance in stress-corrosion testing techniques (23). Using these concepts it is possible to specify a "stress-intensity" K_I at the tip of a crack (which depends on the applied load, the specimen geometry and the crack dimensions), in a high-strength notch-sensitive material. In a smooth, un-notched specimen the analogous parameter is the applied stress σ (which depends on the applied load and the specimen geometry). Similarly it is found that a material constant exists for a particular high-strength alloy, known as the fracture toughness K_{Ic}, which may be crudely defined as the stress intensity required at a crack tip to initiate rapid fracture. Again, the analogous material constant for a smooth unnotched specimen is the tensile strength, σ_{tu}. The advantages of these concepts are twofold. Firstly, they permit laboratory testing of fatigue-pre-cracked specimens, which largely eliminates uncertainty as to the extent of t_i. Secondly, it turns out, for very many alloy/environment systems, there is an applicable system constant designated $K_{Is.c.c.}$ ($\ll K_{Ic}$); this is the applied stress intensity K_I below which it is observed experimentally that stress-corrosion cracks will not propagate. Examples of typical stress-corrosion specimens (after testing) which were designed to make use of fracture mechanics concepts are shown in Fig. 3. Thus it is possible for the research metallurgist to study crack propagation unambiguously and to give the design engineer a stress intensity, with units of [stress] x [length]$^{1/2}$, which should not be exceeded at the tip of any flaw or crack which is likely to develop or exist in a component. The values K_{Ic} and K_{Iscc} are also applicable to fail-safe design methods. The net result is that it is possible to use high-strength structural materials, which can be highly susceptible to stress-corrosion cracking under certain conditions, for advanced space and hydrospace applications with comparative safety. The basic philosophy behind this use is that one can not prevent the existence of flaws but one can ensure that they do not grow to critical lengths by a stress-corrosion mechanism. This is, of course, a very conservative design philosophy but, in the present understanding of stress-corrosion cracking, and in applications where human safety is relevant, it is perhaps the only one ethically justifiable.

II. 8. Phenomenology of Stress-Corrosion Crack Propagation.

Phenomenologically, stress-corrosion cracks are observed to propagate by two different paths, intergranularly (e.g., aluminum alloys and high-strength steels) and transgranularly (e.g., stainless steels). In general, a particular alloy exposed to a particular environment will always show the same crack morphology. However, relatively small changes in alloy (heat-treatment or composition) or environment (pH for example) may result in a transition from inter-to transgranular crack growth or vice versa. The absolute crack growth rates may vary from

extremely slow ($\sim 10^{-7}$ cm/sec.), through the typical stress-corrosion crack growth rate range of 10^{-4} - 10^{-2} cm/sec, to very rapid (up to $\sim 10^{3}$ cm/sec. for liquid metal embrittlement). Examples of intergranular and transgranular stress-corrosion cracks are shown in Figs. 4 and 5.

II. 9. Theories of Stress-Corrosion Crack Propagation.

The majority of workers in the field of stress-corrosion today are more or less agreed that no single mechanism of stress-corrosion crack propagation exists which is applicable to all alloys in all environments; even this statement, however, would not find general acceptance. It is an understatement to say that there is no specific mechanism for crack propagation in any particular alloy/environment system which is generally accepted. Possibly a better name for the phenomena would be environmentally-induced sub-critical crack growth; this accurately describes and embraces stress-corrosion, hydrogen-embrittlement, static fatigue, liquid metal embrittlement, stress-crazing etc. (i.e. almost all alloy/environment systems) without any pretence of specifying or understanding a mechanism or implying that there is a single one.

In the time available it will only be possible to mention briefly some of the more plausible types of mechanism for sub-critical environmentally induced crack-growth. These are:

(1) Stress-sorption: It is assumed that ions, atoms or molecules (depending on the active corrodent species in the environment) are adsorbed (by some unspecified mechanism) onto the metal surface at the crack tip. The resultant electronic interactions weaken the tensile fracture stress σ of the metal-metal bonds at the crack tip while electronic shielding prevents the shear stress τ in the bulk of the alloy being significantly affected (24). Thus the ratio σ/τ is decreased which leads to an increased tendency towards brittle cleavage failure at low stresses (25). It is probable that this mechanism applies to liquid metal embrittlement and possibly also to a number of other cases of stress-corrosion cracking.

(2) Hydrogen-embrittlement: Some electrochemical corrosion reaction is involved in a large proportion of all cases of stress-corrosion cracking; this is most simply demonstrated by the fact that application of a cathodic or anodic potential to a metal during stress-corrosion usually markedly accelerates or slows down the crack growth rate (depending on the alloy/environment couple) but seldom leaves it unaffected. In cases where an applied cathodic potential accelerates cracking it is assumed that hydrogen, from the cathodic reaction $H^+ + e^- \rightarrow H$, is to some extent responsible for the cracking. The precise mode of action of the hydrogen is not clearly understood but the numerous suggestions include: (i) stress-sorption, (ii) formation of a brittle hydride (in titanium alloys) (26), (iii) development of high hydrogen concentrations in solid solution in the triaxially-stressed region just ahead of the crack tip (27), (iv) formation of high pressure "bubbles" of molecular hydrogen within the metal (28), (v) precipitation of hydrogen at heterogenieties in the metal (29). All these theories assume

the presence of hydrogen from the electrochemical corrosion reaction and attempt to account for the observed tendency towards cleavage.

(3) Repetitive film rupture: It is postulated that some kind of protective "film" is formed at the crack tip. When this film is ruptured, either directly by the applied stress or indirectly by the emergence of a slip step, fresh unprotected metal is exposed. This metal is then dissolved, either chemically or electrochemically, by the environment and in the process the protective film is reformed; eventually the film is re-ruptured, the process becomes repetitive and slow crack growth ensues. The precise nature of the film varies widely; for example, it may be the black CuO "tarnish" formed on brasses exposed to some ammoniacal solutions (6), or it may be a protective nickel-rich layer formed on the surface of stainless steels by selective dissolution of the other components (10).

(4) Electrochemical theories: It is assumed that the tip of a crack is sufficiently anodic to dissolve rapidly enough to account for the observed crack propagation rates. With single phase alloys it is assumed that the crack tip is highly anodic and can sustain high corrosion currents and dissolution rates as the material at the crack tip is being deformed continuously at quite high strain-rates (strain-assisted depolarization) (30). Alternatively, precipitates in the alloy may be highly anodic with respect to the matrix; the resultant selective dissolution of these precipitates leads either to a crack (in the case of a continuous grain-boundary precipitate) or to a weakened porous structure (in the case of discontinuous precipitates). The precipitate-free zone which exists adjacent to grain boundaries in the high-strength age-hardening aluminum alloys is thought to be of great importance in this connection.

Most theories of stress-corrosion crack propagation fall into one of the above categories. The specific theories themselves, however, vary greatly in detail, incorporate ideas not mentioned above and sometimes combine parts of the preceding concepts. Stress-corrosion theorists as a type have an exceptional facility for ignoring inconvenient data and choosing only those which fit their own theory.

II. 10. Conclusion.

In this section an attempt has been made to describe in the most general of terms the common pehnomenological aspects and some of the theories of environmentally-induced sub-critical crack growth in metals and alloys. The field is too vast even to begin to consider here any specific alloy-environment system in detail. Such particular experimental results as are included will be found in the final section. In this section the references given tend, in most cases, to be the latest review articles or, alternatively, papers containing particularly original ideas or results; it is intended that these should serve as a starting-point for any more detailed study that is attempted.

III Changes Produced in the Surface Layers of Metals by Machining and Grinding Operations

III. 1. Introduction.

Papers presented earlier at this conference have considered in some detail the physical and chemical changes produced in the surface layers of metals by machining and grinding operations. Indeed, the scattered nature of the data and the dearth of recent review papers on these topics (prior to the above-mentioned), a state of affairs which made itself particularly felt during the preparation of this review, emphasize the need for this conference. In spite of these papers, however, it is considered necessary at this point to discuss again these changes, but from the point of view of their relevance to stress-corrosion crack initiation. This should not be too repetitive.

III. 2. Undamaged Surfaces: Types of Surface Damage.

Before considering any changes that may be produced in metal surfaces by machining and grinding, it is useful to define as a baseline an "undamaged" metal surface. Consider an undamaged metal surface to be "smooth" (i.e. highly polished by either mechanical or electrochemical techniques) flaw-free and covered with a very thin more or less adherant oxide film. The metal layers immediately below the surface contain no residual stresses and are indistinguishable from material far-removed from the surface with respect to vacancy concentration, dislocation density and structure, precipitate distribution, grain size, degree of cold work etc. This is obviously a somewhat arbitrary definition but it is of some use as a starting point. It is equally obvious that this ideal surface can only be obtained by quite specialized metallographic techniques and that it would seldom be encountered in practice. In particular real surfaces usually contain some degree of machining, grinding, or other forming damage. In addition, there is a growing technological tendency to have the surface layers of a component significantly different in some respect from the interior. The techniques of carburizing, shot-peening, plating etc, can not be described as new; it would appear possible, however, with the development of "metalliding" processes in France and the U.S.A. (31), that a new range of "surface-composite" materials with very novel properties will become available in the near future. These may present problems to machinists but they may also have greatly improved stress-corrosion resistance. It has recently been shown for example, that nitriding stainless steels, to produce a surface layer of CrN, significantly delays the initiation of stress-corrosion cracks (32).

Given the above definition of an ideal surface, it is possible to distinguish three broadly different types of damage or change that may be introduced by machining or grinding. These are physical (i.e. mechanical or geometrical) damage, structural changes and compositional or chemical changes. These three categories will now be considered individually.

III. 3. Physical (Mechanical and Geometrical) Changes.

One can distinguish three types of physical damage that may be produced in a surface by machining or grinding. In order of increasingly deleterious effect on stress-corrosion resistance, these are surface roughening, generation of tensile residual stresses in the surface, and micro-crack formation. These three types of damage will be considered separately.

(1) Surface-roughening: An initially smooth surface, with a profile as shown in Fig.6 (a), will typically have a profile more or less as shown in Fig. 6 (b) after machining or grinding, (In practice, of course, this profile is approached from a "rough" and not a "smooth" state, by machining or grinding an over-size component). This profile may be divided into three components, the "roughness" (primary texture), shown in Fig. 6 (c), the waviness (secondary texture) shown in Fig. 6 (d) and an "error of form" shown in Fig. 6 (e) (33). Time does not permit a discussion of the various ways which have been suggested for specifying these components quantitatively and in three dimensions. Clearly, however, only the "roughness" will have a significant effect on stress-corrosion crack initiation and qualitatively, the "deeper" "steeper" and "sharper" the roughness component "valleys," the more deleterious will be their effect as stress-raisers.

(2) Residual stresses: It is well known that surface residual streses can have a marked effect on fatigue life and it should be equally well known that bulk residual stress alone can result in stress-corrosion failure. Similarly surface residual stresses can markedly affect stress-corrosion crack initiation. Residual stresses resulting from machining and grinding may be attributable to any, or more commonly a combination of all, of the following three effects:

(a) Thermal effects: The surface layers become hot, due mainly to frictional heating, expand and instantaneous compressive stresses which exceed the compressive yield stress are generated, owing to the restraining effect of the cold bulk of the component. On subsequent cooling, residual tensile stresses are generated in the surface layers by the reverse process. The parameter (temperature rise). (thermal expansion coefficient).(elastic modulus) is a good measure of the instantaneous compressive stress due to thermal effects (34) and hence, indirectly of the residual tensile stresses.

(b) Transformation effects: Phase changes and/or precipitation reactions often result in a volume change which, by a similar sequence of events to those described above, can lead to either tensile or compressive residual stresses in the surface layers. Probably the most important practical examples of this effect are the tempering, hardening (martensite-formation) and austenite-reversion reactions which can occur in steels. It is clear that which reaction predominates depends largely on the temperature rise, the time at temperature, and the cooling rate; little else, however, is clear and predictions as to which reaction predominates under a particular condition, and the resultant stresses, are impossible at present.

(c) Mechanical effects: Non-uniform plastic deformation of the surface layers during machining or grinding, as compared to the bulk of the material, produces residual stresses which may also be either tensile or compressive. These residual stresses usually predominate at the extreme outer surface layers.

As a general rule, any tensile stresses at or near the surface of a component will have a deleterious effect on stress-corrosion resistance and are therefore undesirable. Conversely any compressive stresses will have a beneficial effect, hence the general efficacy of various types of peening treatment in preventing or mitigating stress-corrosion cracking. Also the more abusive the grinding or machining, the blunter the tool etc., the greater will be the magnitude of the residual stresses.

The extreme surface residual stress in steels (i.e. that component due to mechanical effects) after grinding may be either compressive or tensile, depending on the grinding conditions. Obviously, the former is desirable, but even in this case the residual stresses some way below the surface (due to thermal effects) will be tensile (35). The extreme surface residual stresses in machined steels appear almost always to be tensile (36) and hence tensile stresses exist from the surface inwards, an undesirable state of affairs. No information on surface residual stresses in materials other than steels seems to be readily available. Information on other surface treatments is scant; in lapped or abraded surfaces the residual stresses may be compressive (37). In general, electrochemical metal removal methods introduce no residual stresses unless sparking or some form of abrasive cutting is also involved when tensile residual stresses may result in the surface (38).

It is apparent that cutting-fluids which are good lubricants will reduce the frictional heat generated and hence have a beneficial effect on the magnitude of the residual tensile stresses in a surface due to thermal effects. Care should be taken, however, in choice of cutting-fluid and also in choice of solvents for degreasing and cleaning components as it has been shown that stress-corrosion cracks will propagate in high strength steels (38) and in titanium (39) and aluminum alloys (40) in many organic liquids.

(3) Micro-crack formation: Conventional machining or grinding of conventional materials should not result in microcracks; the same, however, is not true of highly brittle materials or materials which cleave easily, in which case cracks may result. Similarly microcracks may result in ductile materials after machining by non-conventional techniques; spark-machining, for example, produces surface cracks in W, Rh, Zn, Cu and Fe - 3% Si (41). The presence of any micro-cracks in the surface, could, of course, have a disastrous effect on stress-corrosion resistance.

III. 4. Structural Changes.

Most of the structural changes, with respect to the original ideal

surface, which exist after machining or grinding a metal surface may be attributed to the existence of plastically deformed layers near the surface; temperature effects seem to play a less important role. Two distinct zones can be recognized in the plastically deformed layer: these are an outer fragmented layer of severe deformation and an inner layer of minor deformation (37). Owing to experimental advantages, these layers have been most extensively studied in brasses, but some work has also been done on other alloys.

The outer, heavily-deformed, layer follows closely the contours of the surface and its thickness is of the same order as the amplitude of the roughness component of the surface topography. This layer may be detected metallographically, in many cases, on taper sections. Electron diffraction experiments have shown that the extreme outer layer consists of small, coherent, randomly-orientated fragments. This layer is removed by a light etch and material which is still fragmented but much less severely misorientated and deformed is revealed. The properties of these layers may approximate to those of very fine grain-size heavily cold-worked materials. The effect this thin layer would have on stress-corrosion crack initiation is not clear; in any case, any effect would almost certainly vary from (alloy/environment) system to system.

The inner, midly-deformed, layer constitutes the bulk of the deformed material; it can be detected metallographically only when evidence of mild plastic deformation can be revealed by special etching techniques. The plastic strains in this region (typically of the order of 5% in brasses) are usually very inhomogeneously distributed; in brasses they are concentrated in rays extending beneath individual surface scratches (37) with areas of slight deformation between and below the rays. In brasses the overall depth of the plactically deformed layers may be up to 50 times the depth of the surface scratches which, in turn, may vary from 0.1 to 5 μ or more, depending on the severity of the surface treatment. The depth of the deformed layer may be expected to vary inversely with the hardness of the material. Thus the depth of the deformed layer is usually somewhat less than the depth of the layer of metal which contains significant residual stress; this latter may vary from 25 to 500 μ in steels (42). However, the plastic deformations, like the residual stresses, are additive so that a subsequent operation will lead to further damage unless all the damaged layers from the first operations are removed by the second; this latter does not usually occur in practice.

To summarize the above, the surface layers of a metal after machining or grinding are deformed, the outer layers being most severely worked with the plastic strains becoming steadily less at increasing depths below the surface. The severity of the deformation increases with the abusiveness of the surface operations. Except at the extreme outer surface, where there could be hot-work most of the deformation probably occurs as cold-work. The presence of plastic deformation and cold work can affect

stress-corrosion cracking in some alloys. In addition the following effects may result from the plastic deformation and these in turn may also affect stress-corrosion susceptibility:

(1) Vacancy concentration: Plastic deformation greatly increases the concentration of vacancies (and, to a lesser extent, the concentration of interstitialcies and other point defects) in a metal. This in turn leads to altered diffusion rates, especially at room temperature; this effect could be important if diffusion of some species (in particular, hydrogen) into and in a metal is required for crack initiation and propagation.

(2) Dislocation concentration: Cold work increases the dislocation density in a metal by orders of magnitude; in other words, the material becomes work-hardened, with all the changes in mechanical properties that this implies. Dislocations are involved in various ways in many theories of stress-corrosion cracking and it has been experimentally observed that planar dislocation arrays are often associated with a high degree of stress-corrosion susceptibility in a number of different metals and alloys (127)

(3) Twinning: Non-cubic metals show mechanical twin formation in the plastically deformed surface layers (43).

(4) Slip: As the metal is plastically deformed, slip bands will exist throughout the layers adjacent to the surface; these will, of course, also be inhomogeneously distributed.

(5) Recrystallization: In low melting metals such as tin, zinc and lead, the plastic strain, combined with the temperature rise, may be sufficient to cause recrystallization (43); as usual, the extent to which this occurs is very dependent on the grinding conditions and its effect on stress-corrosion crack initiation cannot be predicted. In higher melting metals, heating in service after machining or grinding may be sufficient to cause subsequent recrystallization.

To conclude, therefore, it is possible that any or all of the above effects, which result from the cold-work and plastic deformation inherent in machining and grinding processes could affect stress-corrosion crack initiation in a particular alloy/environment system. The present state of theoretical and experimental knowledge, however, does not permit any specific predictions to be made.

III. 5. Compositional and Chemical Changes.

In this section those changes due to machining or grinding a metal surface which result in the presence of a phase which has a different crystal structure or composition from the bulk of the metal are considered. More than ever, the precise changes which occur are dependent on the alloy concerned and the surfacing conditions (i.e. temperature rise, time-at-temperature, cooling-rate, extent of plastic deformation etc). Any resultant effects on stress-corrosion susceptibility,

are therefore correspondingly dependent on the surfacing conditions as well as on the alloy/environment system under consideration and, in the absence of experimental data, the precise nature of any effect is largely a matter of conjecture. Furthermore, these effects may be due to mechanical differences between the newly formed phase and the matrix, electrochemical differences, or to the inherently susceptible nature of the phase itself. The general types of change which have been observed to occur are as follows:

(1) Embedded particles: There is an observed tendency for abrasive particles from the tool to become embedded in the work piece; this is particularly evident during the grinding of soft materials. These embedded particles may exert a deleterious effect on stress-corrosion resistance either by acting as stress-raisers or by having markedly different electrochemical properties from the matrix.

(2) Surface films: The nature of the surface film on a metal component (usually an oxide film, of course) may be markedly changed by machining or grinding. The film may be thickened and made more protective or weakened and made less protective; alternatively the interaction of dislocations with the surface may be altered significantly, leading to different mechanical properties.

(3) Strain-induced transformations: The classic example of strain-induced transformation is that which occurs at room temperature in 18/8 stainless steels; this is a martensitic-type transformation which results in lamellae of a ferritic phase. It has been observed to have occurred adjacent to ground stainless steel surfaces (44). Similar transformations are also observed in other metastable alloys such as β-brass and Cu-Si. As an example of the interplay between conditions, however, excessive temperature rise may prevent these transformations occurring.

(4) Temperature-induced transformations: As mentioned previously, the most important phase changes resulting from the temperature rise which occurs during machining and grinding are those observed in steels. Typically, a quenched and tempered steel may have a hard "white" layer of untempered martensite at the extreme surface and an inner soft layer of over-tempered martensite. Altering the severity of the surfacing conditions can result in the elimination of either the hardered or softened layer or, under optimum conditions, of both. It would appear that the time at temperature is too short for significant decarburization to occur. Under highly abusive conditions the depth of the "white" layer can exceed 0.002 ins. (42). These however, are by no means the only transformations that can occur; high temperature phases in other alloys may be retained by the very rapid cooling which usually occurs after the temperature rise. Age-hardening alloys may overage and soften. Recently, resolutioning and precipitation of acicular alpha has been observed adjacent to the machined-and-ground surface of aged Ti-6Al-4V alloys (45).

(5) Liquid metal: Melting of the metal at the surface during conventional machining and grinding does not appear to be common and the existence of a Beilby layer (an extreme surface layer of amorphous material produced by "smearing") is not considered probable (37). However, during electrical-discharge-machining, some melting does occur and sputtered droplets of molten metal, which presumably solidified under extreme conditions, are observed on the machined surfaces.

To conclude this section, mention should be made of the possibility of a chemical or electrochemical reaction occurring between the cutting-fluid and the work-piece and/or the tool, leading to general corrosion or to pitting or to intergranular corrosion. Alternatively, adsorbed surface layers of some components of the cutting-fluid could result.

III. 6. Conclusion.

An attempt has been made to discuss in this section the types of damage and change that are produced in the surface layers of metals, by machining and grinding operations and which, under unfavorable conditions, could have a deleterious effect on stress-corrosion resistance.

IV. Review of Experimental Results

IV. 1. Introduction.

Such is the paucity of data that it is possible to review in this section most of the readily-available published experimental results on the effect of surface preparation on the stress-corrosion susceptibility of the six most important classes of alloy (brasses, titanium alloys, aluminum alloys, high strength steels, stainless steels and carbon steels). It is hoped that this section may be of some practical use as it stands; it will certainly highlight the urgent need for further research into the problem. Where possible, reference will be made to the ideas developed in the previous two sections.

IV. 2. Copper-Base Alloys.

Although season-cracking in copper-zinc alloys was the first case of stress-corrosion of practical importance, the phenomenon of stress-corrosion cracking in brasses is still by no means fully understood. In practice damp ammoniacal atmospheres, inter alia, cause stress-corrosion in brasses while in the laboratory tests are usually carried out in aqueous solutions containing ammonium or cuprammonium ions. Most other copper base alloys, in addition to the Cu-Zn brasses, are also susceptible to stress-corrosion under suitable conditions (7) and even pure copper is rendered susceptible by traces ($>0.004\%$) of phosphorus (46); however, nickel bronzes containing $>20\%$ Ni have been reported to be immune (47). The effect of cold-work on the susceptibility of brasses to stress-corrosion is complicated; a small amount of cold-rolling makes

the alloy somewhat more susceptible (48) but as the degree of cold-work increases, the susceptibility decreases again (49). On the other hand, the time-to-failure of brass specimens increases as their grain size decreases (49, 50). The crack path in brasses is generally intergranular in α - alloys, transgranular in β alloys while in α-β alloys the cracks grow intergranularly with respect to α-grains and transgranularly across β-grains (7); many exceptions to these generalizations have been reported however. The phenomena of stress-corrosion in brasses are extremely complex and recent papers suggest that at least three different mechanisms may be operative (6). In some ammoniacal solutions, for example, α-brasses "tarnish" and a black film, which is predominantly cuprous oxide, is formed; in this case a film-rupture mechanism is postulated. In other cases, however, films do not form and mechanisms involving stress-sorption or dissolution reactions are suggested (6).

In spite of the fact that stress-corrosion of brasses has been a practical problem for many years, apparently no comprehensive investigations of the effect of the surface condition on the stress-corrosion susceptibility have been undertaken. Sedricks and Pugh (51) stressed 70-30 brass tensile strips in tarnishing ammoniacal solutions; abrading the surface of the specimen with various grades of SiC paper in both longitudinal and transverse directions resulted in no significant differences in the times-to-failure as compared to polished specimens. Other workers (52) have also observed that various mechanical treatments of the surface, as well as electropolishing or pickling with sulphuric acid, do not alter the susceptibility to stress-corrosion of brass in ammonical solutions. On the other hand, some early work (53, 54) has suggested that polishing brass may have a beneficial effect on the stress-corrosion susceptibility but it has been suggested that these results are not conclusive (55). To summarize, therefore, very little work has been done on the effect of machining, grinding or other surface treatments on the stress-corrosion of brasses and such results as have been obtained are contradictory; on balance, however, it would appear that such treatments do not have a significant effect.

Only methods of mitigating stress-corrosion which involve altering the state of the surface layers of a metal component will be considered as it is suggested that only these methods are relevant to the problems introduced by machining and grinding metals. Discussion of alloy substitution, environment control, surface coatings (a change of environment, in effect) etc. is omitted. The two most important practical methods which are relevant are stress-relief and various peening and polishing treatments. There is little doubt that stress-relief by a low temperature (200-300°C) annealing treatment has considerably reduced the incidence of season-cracking (55, 56) in a number of instances. Shot-peening is a very common method for preventing stress-corrosion in other alloy systems (see below) but for some reason the technique has

not been extensively investigated in the case of brasses. Knight (57) reported that shot-peening increased the time-to-failure of cold-drawn 70-30 brass stressed in 1% $HgNO_3$ solutions from 2 to 100 hours. (Strictly speaking, exposure of brass to mercurous nitrate solutions results in liquid metal embrittlement but it is recommended (58) as a test for susceptibility to stress-corrosion in brasses). Further evidence on the effects of shot-peening brass is sparse (55).

Clearly the predominant effect of shot-peening in any alloy is to introduce residual stresses of a compressive nature into the surface layers of a component; this in turn increases greatly the time required for stress-corrosion crack initiation. However, shot-peening also results in a number of other concomitant effects which should be considered before a shot-peening treatment is recommended:

(1) A dimpled surface results and in extreme cases individual dimples can act as stress-raisers; surface contamination of varying severity also results.

(2) To produce the residual compressive stress, considerable cold work is required; in some alloy systems the susceptibility to stress-corrosion may be increased markedly by cold work.

(3) The residual compressive stresses in the surface layers must be balanced by tensile stresses in the bulk of the metal. Although these latter stresses are usually negligible this may not always be the case, especially in thin sections. A corrosion pit or crevice which penetrates the outer compressive layers is thus exposed to a residual tensile stress, and rapid stress-corrosion crack propagation may follow.

Similarly stress-relief should be used with care. Too high a temperature can result in recrystallization and softening and there is some evidence that the beginnings of recrystallization may be associated with an increase in stress-corrosion susceptibility in brasses (59, 60).

IV. 3. Low-Carbon Steels.

Stress-corrosion occurs in low-carbon steels primarily when these alloys are exposed to hot alkaline solutions (caustic-cracking), to hot or cold nitrate solutions, or to environments containing hydrogen sulphide (sulphide-cracking in "sour" oil wells etc.). Caustic and nitrate cracking are usually observed only in steels containing less than about 0.25%C (7) (pure irons, however, are very resistant to stress-corrosion) while sulphide cracking generally appears to be confined to steels having a hardness of R_C22-24 or more (61). The crack path is intergranular in the case of caustic and nitrate cracking while sulphide cracks probably follow prior-austenite grain-boundaries. Mild steels are susceptible to intergranular corrosion in nitrate solutions in the absence of stress and it appears very probable that the mechanism of stress-corrosion of carbon steels by hydroxides and nitrates, when it is finally elucidated,

will contain a strong electrochemical element. The role of stress is less clear. It is possible that it only involves preventing the blockage of the stress-corrosion crack by corrosion products, but Parkins (9) has suggested that a more important role is probable. The mechanism of sulphide-cracking is thought to involve some form of hydrogen-embrittlement. The effect of cold work on the stress-corrosion susceptibility of mild steel is not clear; some workers have reported an increase in susceptibility (62, 63) while others have claimed a decrease (64, 65). These results may not be completely contradictory, however, as strictly comparable experiments were not undertaken. Similarly the effect of grain size is most complex but it would appear probable that the structure of the grain-boundaries (i.e. the extent of grain-boundary precipitation or segregation) is more important than the grain size as such.

Libert and Hache (66) investigated the delayed failure of L148 carbon steel (0.8% C and 0.66% Mn) stressed at 80% of the yield stress and cathodically charged in sulphuric acid at a current density of 2.5 mA/cm^2. The greatest endurance was shown by specimens which had been shot-blasted and electropolished; these surfaces were marginally better than shot-blasted and unpolished surfaces, but markedly superior to rolled and phosphated surfaces. Athavale and Eilender (63) reported that nitriding a steel increases its resistance to stress-corrosion; this effect was probably due to the compressive stresses produced in the surface layers by the nitriding process; conflicting data on the effect of nitrogen content on the stress-corrosion of carbon steels have been reported. There is ample evidence in the literature (67, 68, 69 inter alia) that stress-relief annealing treatments have a very beneficial effect on stress-corrosion resistance, especially in welded structures. Parkins (70) states that shot-and hammer-peening around welds in various welded steel plates exposed to hot nitrate solutions greatly increased the time-to-failure and in some cases eliminated stress-corrosion completely. Waber and McDonald (71) have also reported a beneficial effect of shot-peening on mild steel exposed to hot nitrates but Champion (72) on the other hand observed no increase in stress-corrosion resistance during service exposure of shot-peened steel tanks exposed to hot caustic solutions.

To summarize this section, no work dealing specifically with the effects of machining or grinding on the stress-corrosion of carbon steels could be located. However, the usual remedies of stress-relief and probably shot-peening are effective in eliminating or mitigating stress-corrosion cracking in alloys of this type.

IV. 4. High Strength Steels

The steels which are considered in this section are such high and ultra-high strength steels as 4340, D6Ac, H-11, 9-4-45, 18 Ni maraging steels, the 400 series martensitic stainless steels etc. Of the high strength steels, the maraging steels have the best all-around resistance to stress-corrosion cracking but it is nevertheless true to say that at present all high strength steels (i.e. those with yield strengths of 200

k.s.i. or greater) are susceptible to stress-corrosion cracking to some extent in all aqueous environments and in many industrialized and marine atmospheres. In some steels, there is marked susceptibility even at strength levels of 180 k.s.i. or less and in a number of cases the strength and stress levels at which high-strength steels can be used are limited by their increasing stress-corrosion susceptibility at high strength and stress levels; this is particularly true in space and hydrospace applications. As high-strength steels are usually notch-sensitive some spectacular and catastrophic failures have been attributed to stress-corrosion in these steels.

The steels are usually used in the quenched and tempered conditions (except, of course, in the case of maraging steels) and the crack path may be either intergranular or (less commonly) transgranular with respect to the prior-austenite grain-boundaries. The susceptibility of these steels is orientation dependent with respect to the longitudinal and transverse directions; however, there is less likelihood of extensive machining exposing unfavorable grain orientations as can occur with aluminum alloys(q.v.). As far as the mechanism is concerned there is still the fundamentally unresolved question of whether an anodic (i.e. dissolution) or cathodic (i.e. hydrogen-embrittlement) process is responsible for the cracking. It appears probable that in fact either may be operative, depending on the alloy and environment conditions; no detailed mechanism is available for either case (7, 11). The effect of prior-austenite grain-size on stress-corrosion susceptibility has not been investigated in detail but preliminary results indicate that it is not marked (73). Stress-corrosion cracks have been shown to initiate at pits formed by localized chemical or electrochemical corrosion in 403 stainless steel (74) and in 4340 (75, 76) alloy steel. In both cases the pits were observed to form predominantly at non-metallic inclusions, particularly manganese sulphide inclusions. For obvious reasons the effect of cold-work on the stress-corrosion susceptibility of high strength steels has not been extensively investigated; thermo-mechanical treatments however, may result in improved resistance.

In contrast to the previous two alloy classes, some work has been done on the effect of machining and grinding on the stress-corrosion susceptibility of high-strength steels but it will become obvious that many apparently contradictory results have been reported and that there is much scope for further work; in particular, very little work has been carried out on fatigue-pre-cracked specimens. Azhogin (77, 78) investigated the stress-corrosion of 30KhGSNA high-strength steel quenched and tempered to $R_C 48$ in an environment of 20% H_2SO_4 + 3% NaCl, using bend-strip specimens. It was observed that specimens with shot-and sand-blasted surfaces had a greater resistance to stress-corrosion (as measured by threshold-stress and time-to-failure parameters) than those with mechanically polished surfaces. Etching the mechanically polished surface in 10% ammonium persulphate to remove 20-30μ of the outer

damaged surface layers resulted in a decrease in susceptibility; electropolishing had a similar effect. Davis (75) on the other hand, working with U-bend specimens of 4330M and 4340, quenched and tempered (1 hr.+1 hr.) at 400°F, and tested by alternate immersion in 3.5% NaCl, reported that electropolishing and chemical-milling increased susceptibility while face-milling resulted in a decrease. Other results obtained by Davis, viz. that shot-peening and sand-blasting increased resistance while grinding increased susceptibility, were in agreement with those of Azhogin. Davis suggested that the residual surface stress was compressive in all cases and that surface treatments which "tear" metal increase stress-corrosion susceptibility while those which "flow" metal decrease susceptibility. A number of other workers have also observed that treatments such as shot-peening, sand-blasting etc. increase the stress-corrosion resistance(115) (usually measured by time-to-failure) of a variety of high strength steels (79, 80, 81). Similarly it seems to be reasonably well established that grinding can be deleterious as far as stress-corrosion susceptibility is concerned; for example, Field and Kahles (42) report that abusive grinding decreased the time to failure of 4340 and D6Ac steels, hardened to R_C50 and tested at a bending stress of 110 k.s.i. in salt spray, from >1000 hours to about 16 hours. Tarasov (82) noted that etching in HCl or H_2SO_4 produced "etch-cracks" almost immediately in the surface of abusively-ground hardened steel while Hildebrand et al.(83) report that the deleterious effect of machining and the beneficial effect of shot-peening on the stress-corrosion resistance of 4340 (quenched and tempered to a tensile strength of 260-290 k.s.i. and tested by alternate immersion in 5% NaCl at an applied stress of 70% σt.y.) persisted even after various surface coatings had been applied in an unsuccessful attempt to eliminate stress-corrosion. Ketcham (84) reports that chem-milled U-bend specimens of H-11 steel were more susceptible to stress-corrosion when tested in 3.5% NaCl than specimens with machine-milled surfaces. This result, which agrees with those of Davis mentioned above, was attributed to the fact that chem-milling results in no surface cold-work and also leaves only very few, but very severe, stress-raisers. Shot-peening of the chem-milled surfaces produced some improvement but not to the level of resistance of the ground surfaces.

The explanation of the conflicting data described above may probably be attributed to the fact that grinding and machining can produce a very wide variety of effects in steels, depending on the working conditions, and in no case were the precise effects resulting from the particular conditions used, fully investigated. For example, Owens (85) reports that surface decarburization reduces the susceptibility of high-strength steels to stress corrosion while Karpenko et al. (86) report that a white layer of untempered martensite on the surface of quenched and tempered 40 Kh steel (specimens produced by different cutting methods) increases the susceptibility to stress-corrosion in 3% NaCl. Turley et al. (80) report that the presence of a layer of untempered martensite on the

surface of 9Ni-4Co-0.45C steel (in both the bainitic and the quenched and tempered martensite conditions) results in increased resistance while the presence of a similar layer on the surface of a 9Ni-4Co-0.30C steel in the quenched and tempered martensite condition results in increased susceptibility. Similarly, these workers found that extremely abusive grinding ("grind-to-burn")produced a very marked increase in the time-to-failure which was attributed to the formation of a protective oxide layer. It was notable that when fatigue-precracked specimens were tested, some conditions which were classed as immune or highly resistant in smooth specimens became susceptible to stress-corrosion cracking. Three other results obtained by Turley et al. are of interest. Firstly the residual surface stresses in various conditions were measured and found to be 70 k.s.i. tensile in as-heat-treated bainite, 20 k.s.i. tensile in as-heat-treated martensite (quenched and tempered), 20 k.s.i. compressive after "standard" surface-grinding and 120 k.s.i. compressive after shot-peening. Secondly, within the bulk of the material the bainite and martensite plates were randomly aligned while near the surface, in the damaged layer produced by grinding, the plates were aligned parallel to the surface. Finally a general relationship between net surface stress (i.e. applied stress + residual stress) and total time to failure was observed; in most cases of stress-corrosion failure in high-strength steels (excluding, of course, fatigue pre-cracked specimens) the initiation time comprises the bulk of the total time-to-failure, which may account for this observed relationship.

It should be borne in mind that in some of the experiments described in this section the failures may have been due to a hydrogen-embrittlement process rather than to an anodic stress-corrosion mechanism (if the two can indeed be distinguished). Fletcher and Elsea (87) report that variations in the mechanical preparation of a steel surface (e.g. grit-blasting, surface-grinding, mechanical polishing, electropolishing etc.) affect the rate of hydrogen permeation (i.e. entry + diffusion) more than can be accounted for on the basis of different effective surface areas. The surface state could also affect the elimination of hydrogen during baking, although here surface films would probably have a predominant affect. It is known also that cold work has a marked but highly complex effect on hydrogen permeation in steel, which could possibly account for the observations of Fletcher and Elsea. For example, Hudson et al. (88) report that the rate of hydrogen absorption during pickling is greater for a heavily sand-blasted than for a lightly sand-blasted steel surface.

To summarize this section published data indicate that machining and grinding operations can have both benefical and deleterious effects on the stress-corrosion resistance of high-strength steels, depending on the surfacing conditions, the alloy and the environment. However, insufficient data are available to allow detailed predictions to be made. It is recommended therefore that until such time as further research does permit reasonable predictions to be attempted with some confidence, the sur-

face-finishing conditons for high-strength steel components be specified as closely as possible and that ad hoc experiments be undertaken to ensure that the conditions specified are, at the very least, not detrimental to the stress-corrosion resistance of the components.

IV. 5. Stainless Steels.

The phenomenon of stress-corrosion has probably been more extensively studied in stainless steels than in any other alloy system, and a correspondingly greater amount of work has been done on the effect of surface preparation on the stress-corrosion susceptibility of these alloys. As in the previous section, however, detailed investigations of the precise changes resulting from closely controlled machining and grinding operations, and the consequent changes in the susceptibility to stress-corrosion, are lacking. The reason for the great amount of attention that has been paid to stainless steels is clearly that until quite recently it was in these alloys that stress-corrosion had the greatest industrial significance.

In the laboratory, stress-corrosion tests on stainless steels are usually carried out in solutions of $MgCl_2$ (approx. 40-45% boiling at 150-155° C). Such an environment presents an extremely severe test of susceptibility and is almost of the "go/no-go" variety; nevertheless, there is good correlation with service experience as far as susceptibility is concerned. In practice, all aqueous environments containing chloride ions must be considered dangerous to some extent, with the probability of stress-corrosion increasing markedly with increasing temperature and chloride concentration. Cracking in stainless steels is predominantly transgranular, although intergranular cracking has been observed, and in many cases there is extensive branching of the cracks. Stress-corrosion cracks have been reported to initiate at MnS inclusions in type 304 stainless steel (89) and there is some evidence to show that the propagation of the cracks is at least partially crystallographic (90 inter alia). There appears to be little doubt that stress-corrosion of stainless steels involves some kind of anodic dissolution process and it is possible that a "film-rupture" mechanism of some type is also an important factor in the overall mechanism (10) but as yet no detailed model for the crack propagation has found general acceptance.

It has been reported (91, 92) that a coarse grain-size increases the stress-corrosion susceptibility of stainless steels but the effect is not spectacular.

The effects of prestrain or cold-work on the stress-corrosion resistance of stainless steels have been the topic of a number of investigations; the effects are complicated and do not seen to be very well established although they may play an important part in the overall effects of machining and grinding on stress-corrosion susceptibility. Greeley et al. (93), using type 302 stainless steel exposed to boiling $MgCl_2$ solutions, observed that the time-to-failure of wire specimens passed

through a minimum at 10% prestrain. The initial decrease in t_f was ascribed to residual tensile stresses while the subsequent marked increase in t_f was attributed to the presence of increasing amounts of quasi-martensite formed by a strain-induced transformation reaction. Very similar results were obtained by Hines (94), using a 18Cr-8Ni-Ti stainless steel, byHawkes et al. (95) using type 316, and by Cochran and Staehle (100) with type 310. On the other hand Burkhart et al. (96), working with type 309 stainless steel, which can not undergo a strain-induced transformation to quasi-martensite as it is not metastable, observed that the time-to-failure decreased progressively with increasing prestrain, up to a value of 30% prestrain; this effect, of course, was attributed to progressively increasing residual stresses. Hochman (97) and Bourrat and Hochman (98) also report that cold-work decreases the stress-corrosion resistance of stable austenitic stainless steels but can increase the resistance of those steels which can form quasi-martensite. Cochran and Staehle however, interpret their results in terms of a dislocation density and interaction mechanism. Somewhat contradictory results were reported by Logan and McBee (99) but these may have been due to the fact that the cold-work was introduced very inhomogeneously by rolling thin strip instead of drawing wires as in the previous cases.

Berge et al. (109) have investigated the effect of surface preparation on the corrosion, as opposed to stress-corrosion, of type 304 stainless steel; this work however is of some interest and may well be relevant to the problem of stress-corrosion initiation in stainless steels. Milled and ground surfaces showed a greater weight loss than electropolished surfaces when exposed to 300°C water, while the electropolished surfaces showed a greater weight loss in 400° C high-pressure steam. These authors report that the milling procedure used produced substantial cold-work to a depth of 10μ, grinding to 5μ, and polishing (with 600 grit paper) to 2μ; furthermore compositional changes in the protective oxide layer were noted after these surfacing treatments.

One of the more detailed investigations of the effect of surface preparation on the stress-corrosion susceptibility of stainless steels was undertaken by Cochran and Staehle (100), using wire specimens of type 310 stainless steel (in which formation of quasi-martensite is not observed) stressed in boiling $MgCl_2$ solutions. The mean time-to-failure of specimens with different surface treatments increased in the order vacuum-annealed (VA) and chemically-polished, VA and mechanically polished (medium), VA and mechanically-polished (rough), VA and electropolished, VA only, and VA and mechanically polished (smooth). The rough, medium and smooth mechanical polishes consisted of 280 grit abrasive paper, grade 0 abrasive paper, and 0.03μ dia. alumina particles respectively. No satisfactory explanation of these results was offered. It was suggested that the scatter of the experimental data may vary with the method of surface preparation. The results reported by other workers show the same general trends as those of Cochran and Staehle. Scheil (101), for example,

testing U-bend samples of 14 different stainless steels reported that specimens pickled in 40% HNO_3-4% HF at 80°C showed no failures, or alternatively showed longer times to failure with less crack formation than specimens polished longitudinally with a No. 120 Aloxite belt. On the other hand Staehle et al. (102), testing type 347 stainless in an autoclave at 400° F, report that pickled specimens and surfaces abraded with a 120 grit belt showed times-to-failure that were approximately equal but shorter than the time-to-failure of electropolished specimens. Birchon and Booth (109), testing austenitic stainless steel at 200-300°C in water containing >10 p.p.m. Cl^- (using an autoclave), observed a threshold strain below which stress-corrosion cracks did not propagate from corrosion pits; this threshold strain was not affected by pickling or electropolishing the specimens, in agreement with the data of Staehle et al. Barnartt and van Rooyen (110) also reported that electropolished surfaces were more susceptible to stress-corrosion than vacuum-annealed surfaces, in agreement with Cochran and Staehle. Other workers have also made less detailed or less conclusive studies (111-113) of the effect of surface preparation.

A number of workers have shown that it is the initiation time only, and not the propagation time, which is affected by surface treatments. Kohl (105, 106) for example, showed that the time-to-failure, in boiling $MgCl_2$ solutions, of tensile specimens of 18Cr/9Ni stainless steel with machined surfaces was one-quarter the time-to-failure of similar specimens with electropolished surfaces. Furthermore, it was shown that the propagation time was the same in both cases, while the initiation time for the machined surfaces was very much shorter than the initiation time for the electropolished surfaces. This effect was attributed to surface cold-work produced by the machining and electrochemical dissolution of 0.3mm. from the surface eliminated it. Hines and Hoar (107) obtained potential-time curves for mechanically polished and fully-annealed 18/8 wires in boiling $MgCl_2$ and noted that the characteristic potential drop (indicating the start of stress-corrosion crack propagation) occurred after much shorter times in the former case; this result also indicates that it is predominantly the initiation time that is being affected.

An extreme effect has been reported by Jackson (114). The surface of an austenitic stainless steel was dry-ground with an abrasive grit; on subsequent exposure to dilute chloride solutions (2 p.p.m. or more), with no applied stress, visible anodic sites formed on the specimen surface at inclusions and subsequently stress-corrosion cracks initiated at these sites. Nielson (103) reported that austenitic stainless steel specimens with 120 grit belt-ground surfaces failed, after approximately 20 minutes exposure to 42% $MgCl_2$, with multiple crack formation; it was noted that the microcracks formed predominantly at 90° to the finishing direction. Specimens belt-ground with finer than 120 grit were resistant to multiple crack formation while sand-blasted surfaces were highly resistant to any

crack formation at all. Overman (89) reports that 304 stainless steel specimens with surfaces dry-ground with a 40 grit abrasive wheel were much more susceptible to stress-corrosion cracking than similar samples with mechanically polished surfaces. Hochman (97) and Bourrat and Hochman (98) observed results in moderate agreement with those already mentioned; the times-to-failure of 18/8 specimens with pickled and mechanically polished-surfaces were very similar, electropolished specimens exhibited a significantly greater time-to-failure while sand-blasted specimens were highly-resistant or immune to stress-corrosion under the testing conditions used. Shot-peening, as well as sand-blasting, also has a beneficial effect on the stress-corrosion resistance of both austenitic and ferritic stainless steels (104).

It is clear that the nature, thickness etc. of the protective oxide film present on stainless steel can markedly affect the stress-corrosion susceptibility (10), but no data is available on how various machining and grinding treatments affect the film itself.

To summarize this section, it is obvious that abusive machining and grinding can have a highly deleterious effect on the stress-corrosion resistance of stainless steels. On the other hand, the standard mitigating treatments such as shot-peening, sand-blasting and stress-relief (116) do produce significant improvements in the resistance of these alloys. In the intermediate region, however, the position is less clear but this fact can probably be attributed basically to differences between what one laboratory and another regard as "light mechanical polishing" etc. The uncertainty as to the effect of cold-work lies partly in the fact that insufficient attention has been paid to the nature of the residual stresses. It is clear that further detailed research is required before the effects of grinding on one hand and shot-peening on the other can be fully understood in the mechanistic sense, i.e. to what extent they are due to residual stresses, to cold-work, to quasi-martensite formation, to oxide-film changes etc. Similarly, no recommendations can be made at present.

IV. 6. Aluminum Alloys.

In service, stress-corrosion cracking is a problem in Al-Mg alloys containing >3% Mg, in Al-Cu alloys, Al-Zn-Mg alloys and in the Al-Zn-Mg-Cu alloys; it is not a practical problem in commercially pure aluminum, or in Al-Mn, Al-Si, Al- < 3% Mg, and Al-Mg-Si alloys, although it can be induced in the laboratory in some of the latter. Thus the 2000, 5000, 6000 and 7000 series aluminum alloys may be susceptible to stress-corrosion cracking in suitable environments; in the case of most alloys, however, non-susceptible or less susceptible tempers (which are often proprietory) have been developed while other tempers (the - T6 temper in particular for example) result in high susceptibility (117). Usually alloys aged to peak hardness are most susceptible to stress-corrosion, while the same alloys in the over-aged condition are generally less susceptible or quite resistant. These alloys have in common the

fact that they are all strengthened on aging by a precipitation-hardening mechanism resulting from the decomposition of a super-saturated solid solution; alloys which are strengthened by cold-work are not generally susceptible to stress-corrosion (7). Environments which can result in stress-corrosion cracking in susceptible aluminum alloys include marine and industrial atmospheres and aqueous environments, especially those containing chlorides.

For practical purposes, stress-corrosion crack propagation in aluminum alloys is invariably intergranular. This, coupled with the fact that the grain-structure in commerical aluminum alloys is extremely stable and difficult to alter, can result in an extremely strong orientation dependence of the stress-corrosion susceptibility. Extrusions of 7075-T6, for example, which typically have a highly directional, elongated grain structure, are effectively immune to stress-corrosion in longitudinal specimens but highly susceptible if short-transverse specimens are tested (118); in general, the greater the anisotropy and directionality of the grain-structure, the greater the orientation-dependence of the stress-corrosion susceptibility. Expressed somewhat differently, a tensile stress with a component normal to the grain-boundaries is required for crack propagation.

It is not possible to generalize as to what differentiates the microstructure of alloys in susceptible tempers from those in non-susceptible tempers. In the 5000-series Al-Mg alloys, for example, maximum susceptibility generally corresponds to the formation of a more or less continuous grain-boundary precipitate of β-Mg_2Al_3 with no intragranular precipitation; this precipitate is markedly anodic with respect to the matrix. In duralumin type alloys (Al-Cu, 2000 series), on the other hand, solute-depleted precipitate-free zones adjacent to the grain-boundaries appear to coincide with maximum stress-corrosion susceptibility; these zones are anodic with respect to both the solute-rich matrix and grain-boundary precipitates of $CuAl_2$ (119). A detailed review of this and other aspects of the stress-corrosion of aluminum alloys has recently been prepared by Sprowls and Brown (117).

It is clear that there is a strong electrochemical anodic dissolution element in the mechanism of stress-corrosion cracking in aluminum alloys. The extent of mechanical rupturing during crack propagation, the role of the tensile stress, and the possible importance of dislocation distribution etc., is less clear. As usual no detailed model or mechanism has found general acceptance.

No information on the effect of grain-size, as opposed to grain-structure, on the stress-corrosion susceptibility of aluminum alloys could be located.

It is well-known that quenching rate from the solution heat - treating temperature and cold-work prior to aging can affect the subsequent precipitation reactions in aluminum alloys, and hence the stress-corrosion susceptibility, very significantly (117). It is thus quite possible

that various surfacing treatments carried out on as-quenched alloys, by virtue of the heating and quenching cycles and cold-work introduced into the surface layers, could markedly alter the subsequent precipitation reaction and thus affect the stress-corrosion susceptibility. Apparently, however, no work has been reported on this topic. Similarly little significant work has been reported on the effect of final machining or grinding operations carried out after aging. In this case, however, it would appear probable that the residual stresses introduced into the surface layers by the finishing operation would predominate, and that any effects of the concomitant cold-work and/or further aging or even overaging (produced by the heating resulting from the machining or grinding) would, in practice, be masked.

Perryman and Hadden (120) investigated the stress-corrosion of tensile strips of Al-2%Mg aged to maximum susceptibility (125°C for 4 hours after 10% prestrain resulting in a continuous grain-boundary precipitate of β-Mg_2Al_3). The average time to failure of as-heated-treated specimens was 3 days. Specimens mechanically polished and etched, electropolished, or pickled showed no change or a slight decrease in time-to-failure; the latter effect was attributed to weakened surface oxide films. Specimens mechanically polished but unetched, shot-peened, or wet-blasted with Al_2O_3 showed increased stress-corrosion resistance (the latter being the best with $t_f > 73$ days); these results were attributed to residual compressive stresses. Farmery and Evans (121) report that the removal of the grey-brown surface film (magnesia + alumina) present on rolled specimens of Al-7%Mg, by pickling in 20% aluminum chloride solution, resulted in a decrease in the time-to-failure from several days to a few minutes. A similar phenomenon was observed in Al-4% Cu alloys and it was suggested that these effects were due to the freshly formed oxide films being superior cathodes.

In a series of papers Hawkes has very clearly demonstrated the effects of residual stress on the stress-corrosion of aluminum alloys. Firstly it was shown that residual microstresses have no effect on the stress-corrosion resistance of DTD 5044 aluminum alloy (122). (Residual microstresses, as opposed to residual macrostresses which have always implicity been discussed heretofore in this review, are those residual stresses which exist within individual grains and across individual grain-boundaries; thus, although the residual macrostress in a component may be zero, both tensile and compressive residual microstresses may still exist within the metal). Secondly, short-transverse cantilever-beam specimens of 5054 alloy were tested, using 0.5 N NaCl solution as corrodent (123); the specimens were treated and aligned so that the highly stressed surface in each experiment (resulting from the non-uniform cantilever-bending loading method used) contained either zero residual stress or a net tensile or compressive residual stress. It was observed that the specimens with zero residual stress had the longest time-to-failure; the specimens containing residual tensile or compressive stresses

showed equal but considerably reduced times-to-failure. The total time-to-failure of specimens containing residual compressive stresses was composed of a long initiation time and a short propagation time while for specimens with residual tensile stresses the reverse situation (i.e. short t_i and long t_p) obtained. The possibility of this effect occurring was discussed briefly in Section IV. 2. Finally (124) it was shown that shot-peening the above specimens resulted in a highly stressed (residual, compressive) surface layer about 0.006 inches thick; all traces of the original residual stresses were obliterated in these surface layers and greatly increased times-to-failure resulted.

A number of other authors have also reported beneficial effects due to shot-peening. Sprowls and Brown (118), for example report that specimens of 7075-T6 stressed at 75% of σ_{ys} with alternate immersion in 3.5% NaCl failed in 1 - 28 days when tested with machined surfaces while shot-peened specimens showed no failure after 365 - 730 days; grit-blasted specimens had intermediate susceptibility. The U.S.A.F. has specified shot-peening treatments for high-strength aluminum alloys and steels for air-craft applications on a number of occasions (125). Jackson and Boyd (126) investigated the shot-peening of 2014-0 and 2014-T6 alloys using steel shot; maximum compressive stresses of about 70% of the yield strength were produced at about 0.003 inches below the surface, while at 0.007 inches below the surface the residual stress was 0-5000 p.s.i. tensile. In general the depth of the compressive layer, in aluminum alloys, was approximately equal to the diameter of the peening shot: it was noted that the use of stainless steel shot resulted in significantly less contamination. The peening treatments increased the time-to-failure in stress-corrosion tests by from x2 to x40; the peening was less beneficial under conditions of alternate immersion, however, as compared to continuous immersion, since the former leads to more serious pitting.

Haynie and Boyd (4) measured the surface residual stress of a 7079-T6 component as-forged as 20 k.s.i. compressive while after machining the residual at the surface was 13 k.s.i. tensile. These authors also stressed the danger of exposing unfavorable short-transverse grain orientations when aluminum alloy forgings etc. are extensively machined; this, in combination with the residual tensile stresses, would have a disastrous effect on the stress-corrosion resistance of the component. Sprowls and Brown (118) also emphasize the point that large forgings should be machined as closely as possible to final dimensions prior to the final solution heat-treatment. Owing to the age-hardening nature of the aluminum alloys which are susceptible to stress-corrosion cracking, stress relief is not usually practical.

It appears from the data available that extensive machining and grinding of aluminum alloys is generally deleterious to the stress-corrosion resistance of these alloys; short-transverse grain orientations are exposed, bulk tensile residual stresses are exposed, and surface residual

stresses are introduced. Research is necessary to determine the least harmful finishing conditions and subsequently these conditions should be very carefully specified. Research is also required to assess the nature and importance of the other changes produced by machining and grinding aluminum alloys and their effect on stress-corrosion susceptibility; in particular attention should be directed to any possible changes in the oxide film.

IV. 7. Titanium Alloys.

Stress-corrosion cracking occurs when titanium alloys are exposed to at least three fundamentally different types of environment and it is probable that significantly different mechanisms of cracking are operative in each case. This section will therefore be subdivided into three parts to deal with each particular case individually.

(A) Hot-Salt Cracking:

When titanium alloys are exposed to elevated temperatures (generally greater than 500°F) under stress, a form of stress-corrosion cracking can occur if traces of salt are present on the surface; oxygen and water vapor are also required for this cracking to occur (8) but these are normally present in sufficient quantities unless special precautions are taken to eliminate them. It should be emphasized at once that although this cracking has been demonstrated in the laboratory under a variety of experimental conditions, no service failures attributable to hot-salt cracking of titanium alloys have been reported (128). All commercial Ti alloys but not commercially pure titanium have been reported to show some degree of susceptibility. The danger of cracking increases with the exposure time, the temperature and the applied stress. The mechanism of this cracking is currently thought to involve some form of hydrogen-embrittlement (8).

Adams (129) states that the time required for onset of stress-corrosion cracking, at a given applied stress level, in specimens of Ti-8Al-1Mo-1V alloy was constant and independent of whether the surface of the sheet specimen was as-received (mill-ground), shot-blasted and pickled, or just pickled. Furthermore, lathe-turned bar specimens of the same alloy were more resistant to hot-salt stress-corrosion than lathe-turned and pickled (in $HF-HNO_3$ solutions) specimens. Heimrl et al. (130) report that 8-1-1 specimens showed no cracking after 6400 hours exposure at 600°F and an applied stress 50 k.s.i. when vibratory cleaning with Al_2O_3 triangles had been employed prior to testing. Glass-bead peened specimens showed no cracking for up to 1000 hours at 600°C while specimens which had been vibratory-cleaned and then had 0.0005 inches removed from their surface by etching exhibited stress-corrosion cracking after less than 100 hours exposure. Braski (131) also reports that peening and vibratory-cleaning improves the hot-salt stress-corrosion resistance of 8-1-1; further, no differences were apparent between 8-1-1 specimens tested as-received and tested with highly mechanically-polished surfaces.

From the very limited data available it appears that shot-peening and vibratory-cleaning enhance the hot-salt stress-corrosion resistance of titanium alloys while the effect of other surface treatments is not marked.

(B) Stress-Corrosion in Non-Electrolytes:

Titanium alloys (in particular Ti-6Al-4V) suffer stress-corrosion cracking when exposed to pure N_2O_4 (nitrogen tetroxide) environments; the mechanism is thought to involve film-rupture and dissolution at slip steps (8). This form of stress-corrosion at one stage was a serious problem in a number of space applications. It was quickly found, however, that traces of the lower oxides of nitrogen (NO in particular) effectively inhibit the cracking. Nevertheless, glass-bead peening is used in addition to this inhibition to protect Saturn S IV B oxidiser tanks.

Ti-6 Al-4V Apollo service module fuel tanks have failed by a stress-corrosion cracking mechanism while being tested under pressure with methanol present as a simulated fuel (132). The presence of about 1% water in the methanol inhibits this cracking, however.

It should also be noted at this point that titanium alloys have been known to exhibit stress-corrosion cracking in fuming red nitric acid (8). No information on the effects of machining or grinding on any of these types of stress-corrosion is available.

(C) Aqueous Environments:

Titanium and its alloys do not suffer pitting corrosion in sea-water or other aqueous environments and in general stress-corrosion cracks will not initiate in titanium alloys in these environments. However, Brown and co-workers (133) showed that stress-corrosion cracks would propagate, in some cases very rapidly, from pre-existing fatigue cracks; stress-corrosion cracking of high-strength titanium alloys in dilute aqueous environments is currently an extremely serious and limiting problem. Alloy chemistry can affect the stress-corrosion susceptibility quite markedly. There is no consensus as to the mechanism of this form of stress-corrosion cracking but electrochemical and hydrogen-embrittlement models are currently popular. It should be noted in conclusion, that a few cases of initiation of stress-corrosion cracks in titanium alloys in aqueous environments have been reported (7).

Very little work has been reported on the effects of machining or grinding. Brown (134) has emphasized the dangers inherent in degreasing Ti alloy components in organic chlorides such as trichlorethylene prior to heat-treating; stress-corrosion cracks are developed during the subsequent heat-treating. Geld and Davang (135) studied the stress-corrosion of Ti-721 alloy in natural sea-water using both notched and fatigue-pre-cracked specimens loaded in 3-point bending; both specimens showed stress-corrosion cracking and some highly significant results were obtained. With the fatigue-precracked specimens, the $K_{I.s.c.c.}$ of steel-shot-peened and grit-blasted specimens was the same as that of surface-ground specimens; in other words, the presence of a fatigue-precrack, as originally intended, minimizes the crack initiation time and ensures that the large

scatter in t_i, attributable to vagaries in the state of the surface, is eliminated. With the notched specimens, however, grit-blasting had no effect on the apparent $K_{I.s.c.c.}$ (i.e. $K_{I.s.c.c.}$ was the same for grit-blasted specimens as for surface-ground specimens), with glass-bead-peened specimens $K_{I.s.c.c.}$ was increased, while with steel-shot-peened specimens the apparent $K_{I.s.c.c.}$ was approximately equal to the apparent fracture toughness, $K_{I.x.c.}$

Sanderson and Scully (136) report that stress-corrosion cracks initiated in smooth tensile strips of Ti-5Al-2.5Sn and Ti-6Al-4V exposed to $MgCl_2$ solutions boiling at 154°C; pitting occurred and subsequently cracks initiated at the very heavily-deformed edges of the sheared specimens. This attack was attributed to damage of the protective oxide film but it is by no means clear that this is the correct or only interpretation of these results. Sanderson et al. (26) report that chemical polishing of Ti-5Al-2.5Sn results in the formation of hydride platelets near the surface; as a result of this reaction stress-corrosion cracks can initiate (at the hydride platelets) in U-bend specimens of this alloy (when chemically-polished) exposed to either boiling $MgCl_2$ solutions or dilute, room temperature NaCl solutions.

Insufficient data is available to draw any conclusions about the effect of machining or grinding on the aqueous chloride stress-corrosion cracking of titanium alloys. It would appear that shot-peening treatments have their usual benefical effect.

IV. 8. Conclusion

In the preceding sections of the paper, an attempt has been made to review as much as possible of the available literature pertaining to the effects of machining and grinding on the stress-corrosion susceptibility of the more common and important alloy systems. Although the data for all systems are clearly very sparse, an attempt will be made in the final sections to draw some general conclusions, to formulate tentative recommendations and to suggest possible approaches for future research.

V. Conclusion

V. 1. General Recommendations.

It is clear from the preceding sections that in the case of no alloy system has the effect of machining and grinding on stress-corrosion susceptibility been sufficiently investigated to justify the formulation of specific recommendations. It is equally clear, however, that in all cases, and particularly in the case of the advanced high-strength alloys, such surfacing or finishing treatments can affect significantly the susceptibility or resistance to stress-corrosion cracking. On balance, the effect usually appears to be more or less deleterious; stated differently, most machining and grinding operations, unless carefully designed and controlled, result in residual surface tensile stress to some extent. These residual stresses

are responsible for the decreased resistance and it would appear that in most cases they mask any effects (either beneficial or deleterious) resulting from the other changes produced in metal surface layers by machining and grinding operations. It should be emphasized that these are only tentative conclusions; further research, as detailed below, is required to confirm, alter or disprove them.

These tentative conclusions, however, have important implications in two areas. Firstly, in both research and development stress-corrosion testing, vagaries in surface preparation can lead to erroneous results and conclusions. This would be especially true, for example, when smooth specimens are being used to establish threshold stresses. On the other hand, pre-cracked specimens would appear to be largely unaffected by the surface finish. It is therefore suggested that more careful consideration be paid to the surface condition, particularly as regards residual stresses, than heretofore seems to have been customary.

Secondly, the finishing treatment used can markedly affect the service performance of metal components as regards stress-corrosion failure. It is suggested that such machining and grinding treatments asare undertaken be specified in much greater detail than appears to be current practice, and that the specified conditions be designed, on the basis of ad hoc experiments, to produce the minimum decrease in stress-corrosion resistance. Finally it must be concluded, possibly with a trace of embarrassment, that shot-peening treatments remain one of the most useful, practical and efficacious methods of eliminating or mitigating stress-corrosion cracking in any particular alloy-environment system.

V. 2. Future Research.

Two avenues of future research appear to be particularly fruitful and necessary. Firstly, using smooth unnotched specimens, detailed investigations are required to correlate the precise changes produced in the surface of a metal by a particular surfacing operation with the resultant changes in stress-corrosion performance. In other words, the surfacing conditions should be accurately and reproducibly known and reported; the resulting physical, structural and chemical changes in the surface layers should be thoroughly investigated; the changes in stress-corrosion susceptibility should be investigated in depth (i.e. with respect to changes in initiation time, threshold stress etc.) and not just with respect to time-to-failure. Some investigations would be of great interest for any alloy-environment system, but they seem to be most urgently required for the stainless and high-strength steels.

Secondly, use should be made of pre-cracked specimens. It is probably widely agreed that the use of smooth, unnotched specimens does not give a valid or safe test of the stress-corrosion performance of high-strength alloys to be used for critical applications. On the other hand, there is a suspicion that the use of fatigue-precracked specimens, as currently designed, leads to overly conservative design criteria; in other

words, the test may be needlessly severe in some cases. Furthermore, it may be argued that too much attention is being paid to minimizing crack propagation and too little to preventing stress-corrosion crack initiation, which may, in the long run, be the more feasible proposition. It is suggested therefore, that specimens be used containing cracks similar to those to be expected or allowed for in practice (say "thumbnail" shaped surface cracks of maximum length 0.10 inches and maximum depth 0.025 inches). Admittedly such testing would be more expensive and time-consuming, and would require more skilled personnel. However, it is possible that it would be a more realistic test; it would certainly allow the effect of various beneficial surface treatments (e.g. shot-peening, possibly decarburization in the case of high-strength steels, possibly the formation of high-nickel surface layers on stainless steels etc.) to be investigated more satisfactorily than at present. It is suggested that this method of testing may be able to be developed to give safe but not needlessly conservative estimates of the stress-corrosion susceptibility of high-strength alloys.

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List of Illustrations:

Figure (1): Catastrophic failure initiated by stress-corrosion cracking in a Ti-6Al-4V Apollo-booster oxidiser-tank exposed to uninhibited N_2O_4 at a stress level of about 80% of the yield stress (Courtesy of E.J. King of Bell Aerosystems).

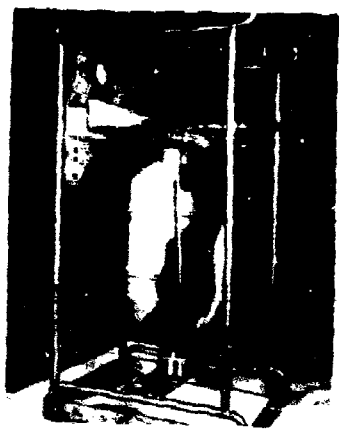
Figure (2): Non-catastrophic failure of a stainless steel autoclave due to stress-corrosion cracking resulting from presence of chlorides in the tap-water used as coolant (Courtesy of R. W. Staehle of The Ohio State University).

Figure (3): Fracture surfaces of fatigue-precracked stress-corrosion specimens after testing. Visible on each specimen are the original saw-cut or notch (A), the fatigue-precrack (B), an area of slow stress-corrosion crack-growth (C) and the final rapid-fracture region (D). Example Y is a double-cantilever-beam long-transverse specimen of 7075-T6 aluminum alloy loaded to an initial stress intensity K_{Ii} of 14.1 k.s.i.$\sqrt{i}$ (approx. 50% K_{Ic}) and exposed to reagent grade carbon tetrachloride for 36,000 minutes. Example X is a cantilever-beam longitudinal specimen of fine-grained A.I.S.I. 4340 steel (quenched and tempered 1 hr. + 1 hr. at 400°F) loaded to an initial stress intensity K_{Ii} of 30.7 k.s.i.$\sqrt{i}$; specimen failed after 75 minutes exposure to aerated 3.5% aq. NaCl at 40°C. Magnification approx. x1.5 (40,73).

Figure (4): Intergranular stress-corrosion cracks in Type 410 martenistic stainless steel (hardened and tempered at 482°C) exposed to boiling 42% magnesium chloride solution for 21.8 hours at a stress level of 100 k.s.i.; magnification approx. x250 (137).

Figure (5): Transgranular stress-corrosion cracks in Type 304 austenitic stainless steel (water-quenched from 982°C and aged at 700°C for 168 hours) tested in magnesium chloride solution boiling at 140°C at an applied stress level of 40 k.s.i.; magnification approx. X250 (138).

Figure (6): Profiles and profile components of smooth and ground surfaces (33).



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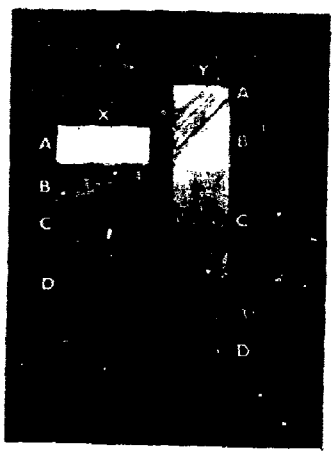

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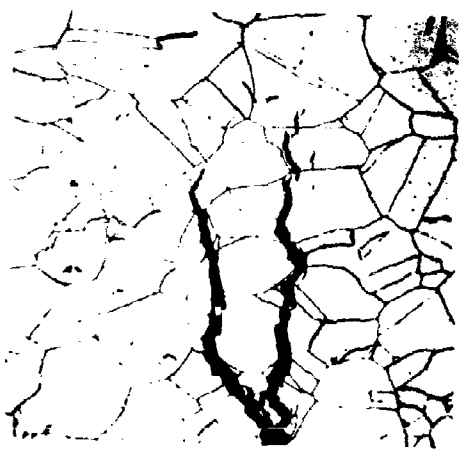

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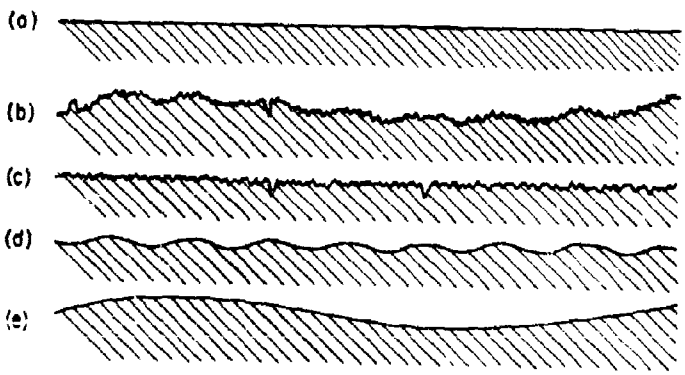

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13. ABSTRACT

A general but necessarily brief introductory review of the occurrence, phenomenology and mechanistic theories of stress-corrosion cracking (in the widest sense of the words), in metals and alloys is provided. Those changes which are produced in the surface layers of metals by machining and grinding operations, and which could conceivably affect the stress-corrosion susceptibility are discussed. A review of the rather scant published data on the experimentally observed effects of machining and grinding on the stress-corrosion performance of the major alloy systems (brasses, low carbon steels, high-strength alloy steels, stainless steels, aluminum alloys and titanium alloy) is presented. The implications of these results as far as stress-corrosion testing and performance is concerned are considered. Finally, some suggestions are made as to the most profitable avenues for future research.

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