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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
NRL Memorandum Report 4807	AD-A114722	

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
LIFE ENHANCEMENT OF NAVAL SYSTEMS THROUGH ADVANCED MATERIALS	Topical report
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
A.I. Schindler and I. Wolock	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Naval Research Laboratory Washington, DC 20375	71056-7600

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research Arlington, VA 22217	May 12, 1982
	13. NUMBER OF PAGES
	49

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Advanced materials	Rotor blades	Laser processing
Fluoropolymer paints	Ion implantation	Corrosion control
Deuterated lubricants	Hot corrosion	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Recent progress in the development of advanced materials to extend the life of Naval systems is discussed. The developments include anti-corrosion and anti-fouling paints, improved lubricants, and more durable helicopter rotor blades, as well as a variety of materials processing techniques and improved uses of materials to reduce corrosion, wear and fatigue of systems components.

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ACKNOWLEDGMENTS

LIFE ENHANCEMENT OF NAVAL SYSTEMS THROUGH ADVANCED MATERIALS

Introduction

Each of the U. S. military services, the Army, Navy and Air Force, has its own unique set of critical factors which influence materials selection and which limit the useful life of deployed military hardware. The overwhelming factor which shortens the lifetime, increases the life cycle costs and decreases the mean time between overhaul for Navy systems is the marine environment. This single factor subjects the materials employed to moisture and salt, and for those systems immersed in the sea, to the degrading effects of marine organisms and fouling. Advanced materials have been developed to address these Navy problems and to provide capabilities that could greatly benefit the other services as well.

A requirement common to all services is that of reliability and maintainability of systems and equipment. The costs associated with maintaining deployed systems at operational readiness can be substantial in terms of both manpower required as well as actual life cycle expenditures. There is a constant requirement to increase the time between overhauls (or failures) but not with the sacrifice of operational capability and reliability. These requirements can be achieved by the application of advanced materials such as those developed for corrosion control, friction reduction, or erosion/wear reduction.

One problem common to all defense establishments is that of aging equipment. Much military equipment, especially planes and ships, is reaching the end of expected useful life. To delay the high cost of replacement, means are being pursued to extend the useful life of existing equipment without sacrificing reliability. This requires the development of advanced materials and processes which can be employed or retrofitted to existing systems resulting in life extension and cost savings. The high cost of new equipment requires that the useful life be extended in order that life cycle costs can be made affordable. Useful life can be extended not only by the use of advanced materials but also by the "advanced" or innovative use of existing materials, that is, by improved techniques for materials processing, evaluation, design, and construction.

In this paper we have tried to touch on some aspect of the materials developments mentioned. We have however tried to be careful in our examples to exclude materials primarily developed for performance enhancement and have concentrated on efforts that will result mainly in life enhancement. Out of the extensive ongoing R & D efforts, we have tried to select a relatively limited but balanced number of examples to demonstrate typical U. S. Navy programs that offer promise of providing life enhancement for military systems.

I. Fluoropolymer Paints

The marine environment contains a number of elements which are exceedingly demanding of paint systems. High humidity in a salt atmosphere tends to promote corrosive undercutting of paint on ferrous surfaces, and the plasticization of paints due to water absorption weakens adhesive bonding. Paints on ship exteriors above the waterline are exposed to photodegradation by direct sunlight and those below the waterline soon become covered with a wide variety of fouling organisms. Ships' interiors pose a problem of cleanliness, particularly in areas such as the bilges, holding tanks, fuel storage and ballast tanks. These are all problems which fluoropolymer paints are uniquely constituted to address effectively.

It is well-known that fluoropolymer coatings have an anti-adhesive property which prevents contaminants from adhering to the coated surface. Present fluoropolymer coating procedures involve sintering at high temperatures, obviously impractical for marine coating applications. However, this process is avoided by the use of newly developed fluoroepoxies, fluoropolyurethanes or fluoroacrylics which can be applied in the manner of conventional paints using typical shipyard equipment. The substantial amount of experimentation that has been done during the last five years on hulls and in bilges and in fuel storage tanks on shore indicates that such coatings are indeed easily cleaned and are very durable.

In addition, the stability of the NRL fluoropolymers is sufficiently great that one would expect exceptional resistance to sunlight (ultraviolet) degradation. The NRL fluoropolymers have been designed so that each carbon atom attached to a fluorine atom is totally fluorinated, resulting in this high stability. Thus paints composed largely of fluorocarbons should exhibit exceptional durability in sunlight and therefore extended life in protecting the underlying surface. Also, these fluorocarbon paints can be designed chemically to provide exceptional wetting of the substrate when applied, and a high degree of hydrophobicity as a cured film. These two factors combine to provide highly corrosion – resistant coatings.

The Naval Research Laboratory has completed basic synthesis efforts on two classes of partially fluorinated polymers, the fluoroepoxies and fluoropolyurethanes. A third class, fluoroacrylics, is in an intermediate stage of synthesis. Within each class, there are a number of individual polymers or resins which retain the normal use conveniences of that particular material type while also possessing a fluorocarbon nature. Thus, the materials can be used in the same manner as conventional epoxies, polyurethanes and acrylics.

Fluoroepoxies

The NRL fluoroepoxies are water-clear liquids of exceptionally low surface tensions which are composed of various levels of stable fluorocarbons up to values in excess of 60% by weight. They are cured by special fluoroanhydrides or by silicone amines to produce, with comparable ease, products analogous to those of the common epoxies. The exceptional wetting capabilities of these

resins allow spreading upon the surface of materials that are difficult to wet such as polytetrafluoroethylene (PTFE). High loading volumes of powdered PTFE can be suspended in fluoroepoxy resins. This allows the production of coatings that retain the convenient characteristics of the epoxies while at the same time imparting PTFE characteristics of wettability. Thus, the coefficients of friction of such coatings are about equal to those of PTFE itself.

Fluoropolyurethanes

The fluoropolyurethane coatings are tough, durable materials that are comparable to the unfluorinated analogs. They have been exposed extensively to the marine environments for more than five years. The results to date strongly suggest that intrinsically superior marine paints can be produced from materials of this class. Most tests to date have been spot trials of available compositions. Concerted developmental efforts to produce optimized coatings are still needed for most applications.

As general coatings, the fluoropolyurethanes offer a number of practical advantages over the fluorinated epoxies, although the latter have special properties which are required in some applications. Generally the fluoropolyurethanes are tougher, cheaper and more convenient to use than the fluoroepoxies. The fluoroepoxies are especially well suited for such applications as adhesives, composite matrix resins, castings and other uses in which neat materials are preferable to those which are solvent-borne, such as the fluoropolyurethanes.

An example of the relative ease of cleaning of a fluoropolyurethane - coated surface is shown in Figure I-1. This is a portion of a ship hull normally below the water line. The dark area shows the fouling that has accumulated. In the adjacent light area, the fouling has been removed by spraying with a fire hose. The coating is still intact and shows no sign of deterioration even though it has been in service for four years and has been cleaned several times using brushes and hoses. This particular service test is still in progress.

Fluoroacrylics

The acrylic class of fluoropolymers differs substantially from the fluoroepoxies and fluoropolyurethanes in several significant respects. Notably, the acrylics can be polymerized readily in linear fashion to produce preformed, solvent-soluble polymers. This eliminates the problem of mixing two or more components shortly prior to application, a procedure which is necessary for both of the other two classes. Unlike the epoxies and polyurethanes, the acrylic polymers contain no polar functionalities within the molecular structures that bear active hydrogen atoms. The favorable consequence of this is that the fluoroacrylic polymers are exceedingly hydrophobic and absorb as little as 0.06% water by weight upon equilibration, which is approximately one-fifth that absorbed by a typical fluoroepoxy. (A typical fluoroepoxy, however, absorbs only about 10% of that of a non-fluorinated epoxy analog). However, the fluoroacrylics are not as tough and adherent as the fluoroepoxies or fluoropolyurethanes. These characteristics considered together suggest that within the fluoro-series, the epoxies or polyurethanes would be preferred for use as original paints, but the acrylics would be more convenient for touchup and repair coatings.
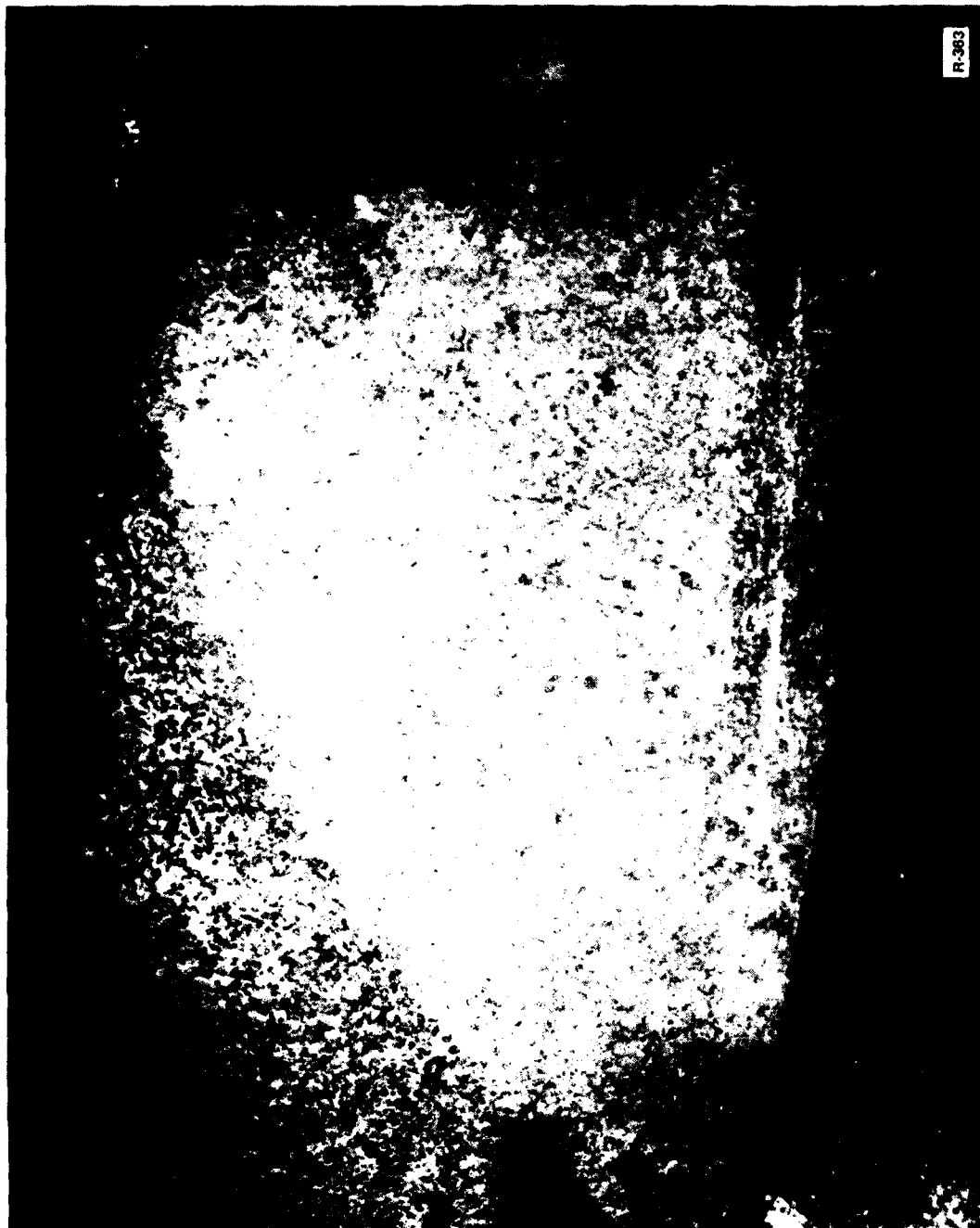
Fig. I-1 — Ships hull coated with fluoropolyurethane. Fouling has been removed (light area) by spraying with a high pressure fire hose. Ship had been exposed to fouling for four years.

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II. Deuterated Lubricants

Present military aircraft gas turbine engines, operating under Mach-2 conditions, can generate bulk oil temperatures of 150°C, oil-out temperatures of 260°C, and short term shaft and bearing temperatures of 300°C under soak-back conditions when the engines are turned off. Current petroleum-based lubricants degrade at these temperatures and the more stable synthetic ester-based formulations are now employed exclusively for this applicaton. In addition to temperature stability, other requirements of a lubricant may be of equal importance. Instrument oils, for example, employed in as little as one - drop quantities to lubricant precision miniature bearings such as those used in guidance systems, must last for the operational life of the mechanisms. Minor changes in viscosity, or the generation of organic particulates resulting from lubricant or additive package deterioration during storage or operation, at high or low temperatures, can result in unacceptable instrument performance or, indeed, failure. A variety of lubricant base stocks is presently employed for the different applications, e.g., petroleum oils, super-refined petroleum oils, modified silicones, esters, synthetic hydrocarbons, etc. Currently, there is a trend towards compactness both for engines with increased power output, e.g., V/STOLS and cruise missiles, and instrumentation. The result is greater heat output, requiring lubricants with enhanced oxidation stability as compared to that presently available. Additionally, even under more benign operational temperature conditions, lubricants with increased stability will result in longer mechanism life, and thus reduced maintenance cost.

Deuterated Synthetic Hydrocarbons

During the last several years, the development of new and improved lubricants has progressed. One novel approach has been the use of deuterated fluids. Based on consideration of the deuterium isotope effect, i.e., more energy is required to rupture the carbon-deuterium bond than the carbon-hydrogen bond, researchers at the Naval Air Development Center postulated that lubricants in which hydrogen was replaced by deuterium should demonstrate a substantial increase in high-temperature stability. Their subsequent investigations showed, (a) that a deuterated synthetic oil (derived from polymerized olefins) was in fact more stable than its hydrocarbon analog, and (b) that a deuterated grease provided a 5-fold increase in bearing life as compared to that of the undeuterated analog. Figure II-1 shows the stabilizing effect in a bomb oxidation test of deuterating a synthetic hydrocarbon. Note that the nondeuterated lubricant begins to oxidize at 20 hours whereas the deuterated material did not absorb oxygen until about 100 hours. Both the hydrogen and deuterium-containing hydrocarbons were prepared by identical methods so as to rule out any purity differences.

Figure II-2 shows the effect on the relative bearing life of progressively deuterating the base stock hydrocarbon component of the grease lubricant. The solid line curve indicates that initial increase in bearing life occurred when the hydrocarbon was about 70 atom % deuterated; when deuteration reached the 97 atom % level, bearing life increased 5-fold over that of the nondeuterated hydrocarbon grease. The earlier data (Figure II-1) suggests that the enhanced bearing performance resulted from the greater stability of the deuterated base oil.
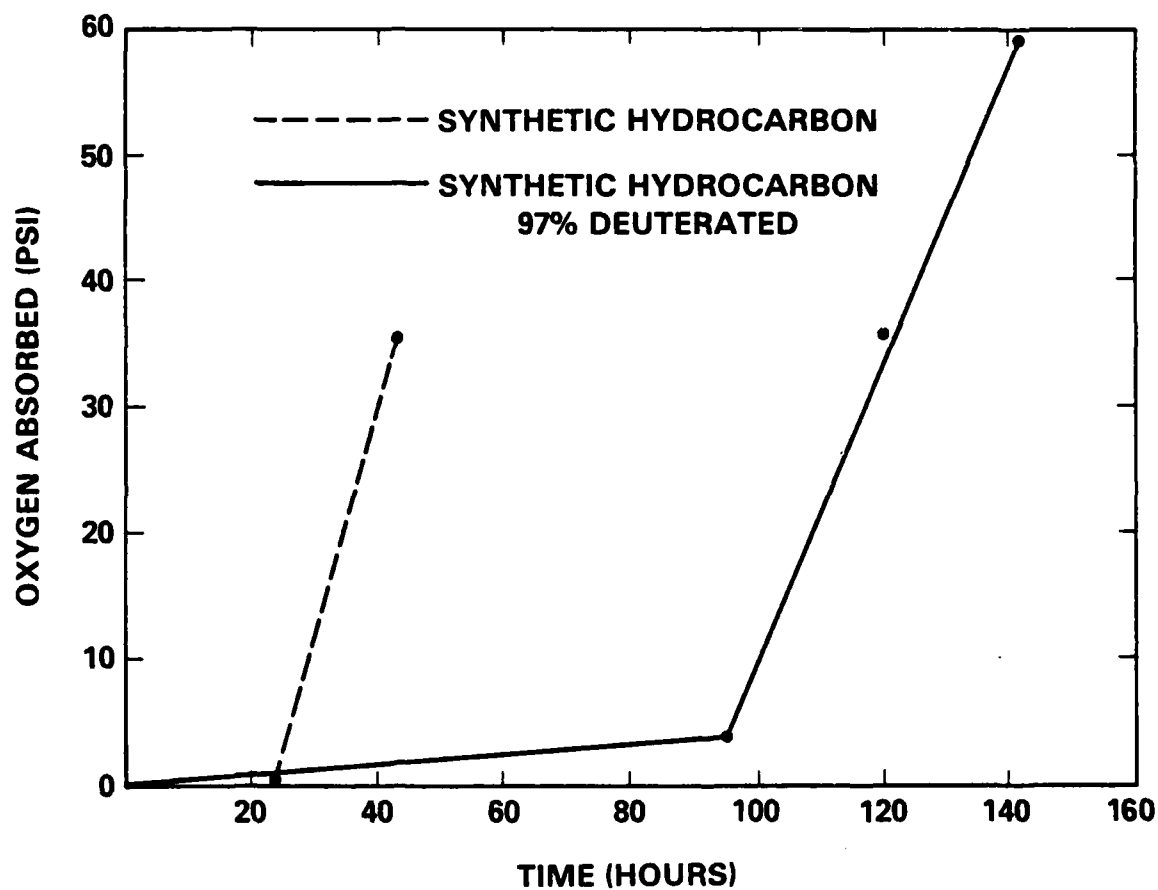
Fig. II-1 — Comparison of stabilities (as measured by oxygen absorbed) of deuterated and non-deuterated synthetic hydrocarbons

BEARING SIZE: SAE 204

LOAD: 13.3N (3 lb) Thrust

22.4N (5 lb) Radial

SPEED: 10,000 RPM

TEMP: 204°C (400°F)

NO. OF TESTS: Avg of at least four runs

BPL NON-DEUTERATED GREASE: 100±30hrs

— △ — ADMIXED

— ⊙ — AS DEUTERATED

BEARING PERFORMANCE LIFE RATIO
(Deuterated vs Non-deuterated Grease)

ATOM PERCENT DEUTERIUM

Fig. II-2 — Antifriction bearing performance life ratios of
lubricants. (NADC Results, 1977)

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Promising as these bearing test results were, however, they were not entirely unambiguous. When equal volumes of nondeuterated and 97 at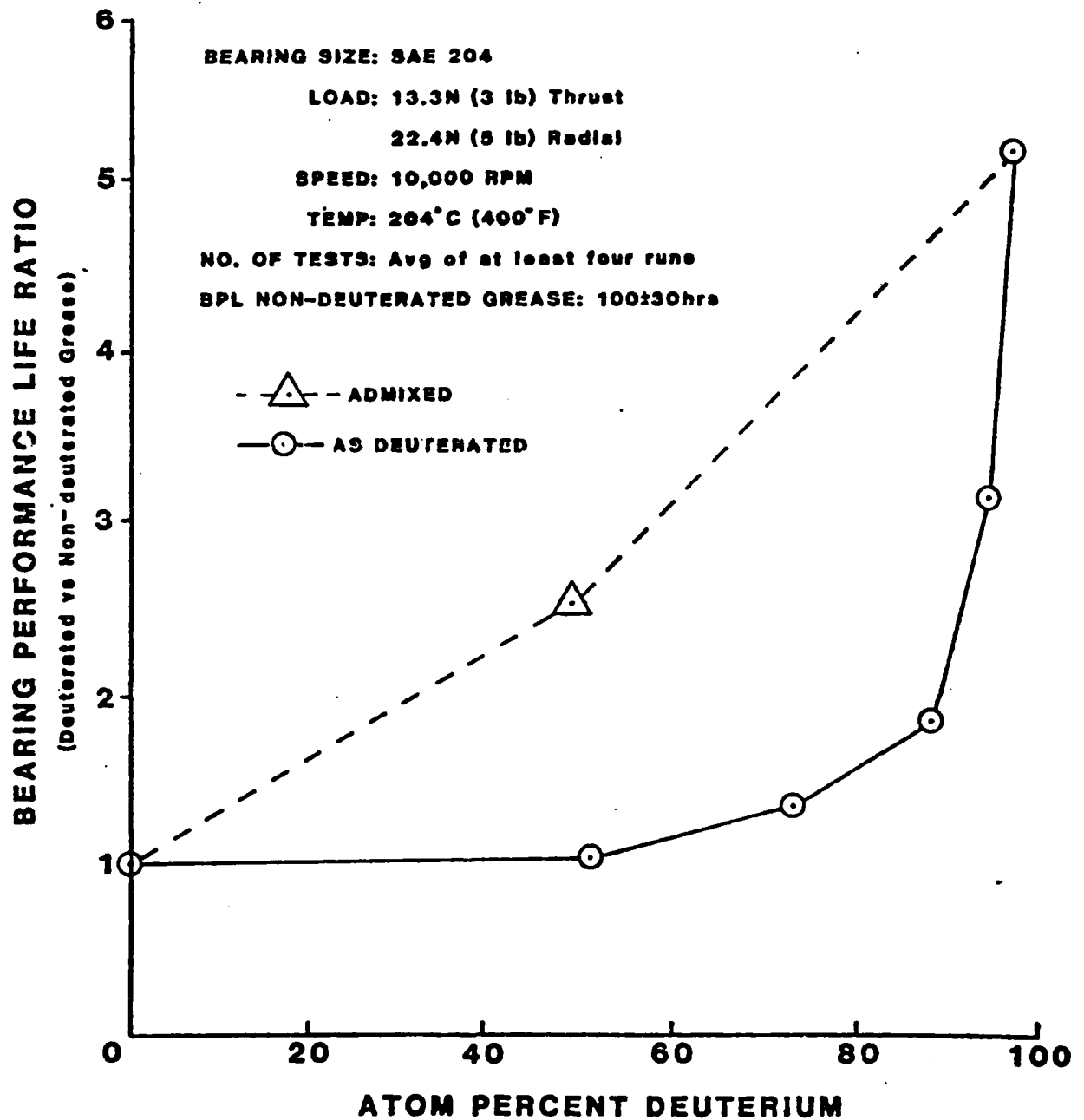om % deuterated fluids were mixed to give an effective deuterium concentration of 49 atom %, oxidation resistance was appreciably less than that of a 51 atom % randomly deuterated fluid. However, as seen in Fig. II-2, performance of the grease based on the admixed fluid was better than that based on the 51 atom % deuterated material (solid line, Fig. II-2). Sufficient data are not yet available to resolve this anomaly. Results of the bearing tests suggest that while oxidation stability of the lubricant may be an important factor in performance, other factors such as contamination and metal catalytic effects, may also play a significant role in lubricant life and bearing failure.

Deuterated Esters

On the basis of these encouraging results by the Naval Air Development Center, the Naval Research Laboratory initiated a program to investigate some of the fundamental reactions involved in the deuteration process and the reactions of classes of deuterated lubricants other than synthetic hydrocarbons, and also, to perform the necessary test and evaluation studies preparatory to field testing those materials. The specific materials selected for this initial study were the neopentyl polyol esters widely used as jet engine aircraft lubricants and instrument oils, because of their excellent response to additives, low volatility, wide liquidus range and outstanding viscosity-temperature characteristics. A representative ester of this class is pentaerythritol tetrahexanoate, which is the basis for the military jet engine lubricant specification, MIL-L-23699.
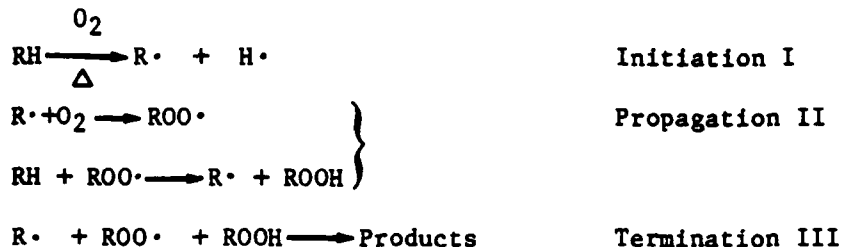
The oxidation stability of this oil, in the presence of an antioxidant, octyl phenyl-1-napthylamine, was compared over the temperature range 200 to 235°C with the partially deuterated analog, pentaerythritol perdeuterotetrahexanoate. Table II-1 shows that even such partial deuteration provided a remarkable 14- to 20-fold increase in stability over that of the undeuterated oil. In the present studies, stable lubricant life was measured by the length of the induction period, i.e., the time required for antioxidant concentration to approach zero, and viscosity, acidity and gas evolution to increase exponentially, Figure II-3. Since it has already been demonstrated that C-H sites on the ester molecule differ in their susceptibility to oxidation, it may be feasible to stabilize by deuteration of only those sites which are most labile. This should serve not only to achieve a significant increase in the stability of the total molecule, but also markedly reduce the cost of the deuteration process.

Table II-1 — Oxidation stability test results as a function of temperature

| Temperature (°C) | Induction Time (Hours) | | Relative Increase in Stability |
	Non-Deuterated Ester	Deuterated Ester	
200	42.4	850.0	20x
220	7.4	102.4	14x
235	0.9	17.2	19x

Deuterated Antioxidants

While the effect of deuteration on the intrinsic oxidation stability of ester lubricants is unquestionably important, antioxidants are almost always included in working formulations to extend operational life. It is generally agreed that the autocatalytic process in most organic compounds proceeds by the following general mechanism:

$$RH \xrightarrow[\Delta]{O_2} R\cdot + H\cdot \qquad\qquad \text{Initiation I}$$

$$\left.\begin{array}{l} R\cdot + O_2 \longrightarrow ROO\cdot \\[1em] RH + ROO\cdot \longrightarrow R\cdot + ROOH \end{array}\right\} \qquad \text{Propagation II}$$

$$R\cdot + ROO\cdot + ROOH \longrightarrow \text{Products} \qquad \text{Termination III}$$

The autocatalytic step, II, can be interrupted by an antioxidant:
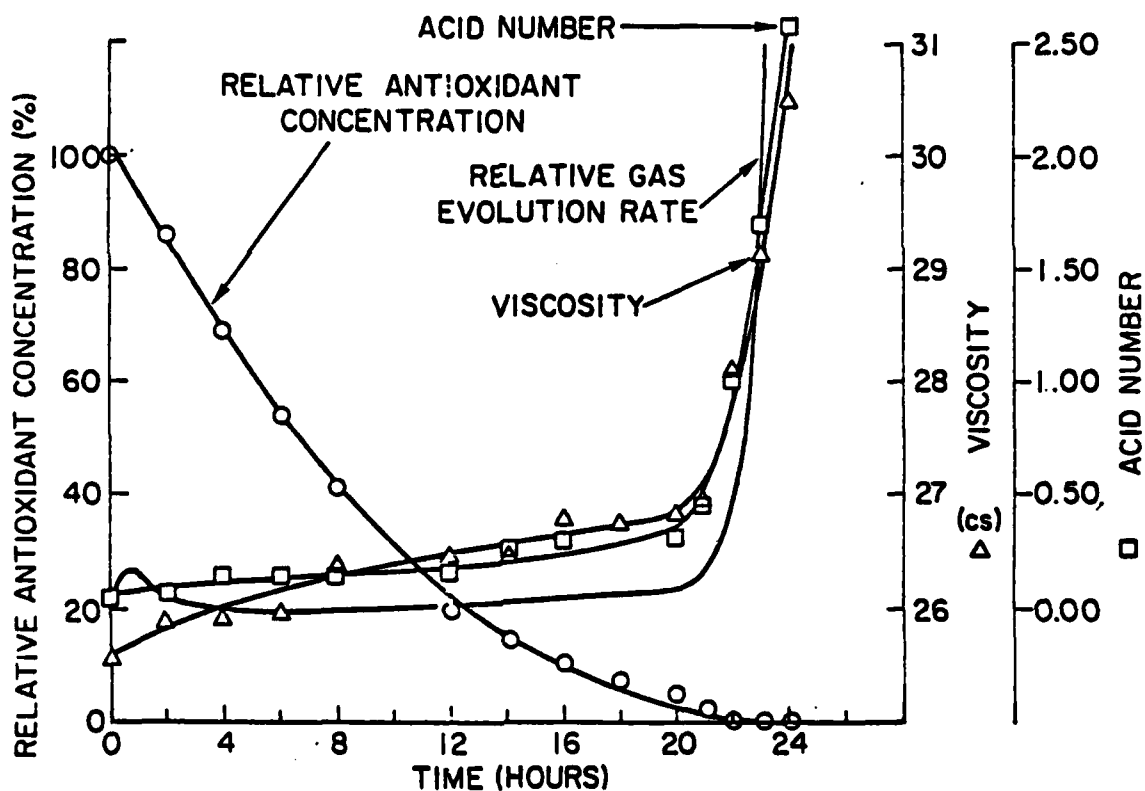$$ROO\cdot + AH \qquad ROOH + A\cdot \qquad\qquad\qquad IV$$

Fig. II-3 — Time required for antioxidant concentration to approach zero and viscosity, acidity, and gas evolution to increase exponentially.

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Here AH represents a generalized antioxidant with H being an active hydrogen atom. It is postulated that the radical A·(IV) is less active than the radical R·(I and II), thus interrupting and slowing down the overall oxidation rate.

Some studies have been made of the deuterium isotope effect on antioxidant activity when deuterium is substituted for the active hydrogen. Since deuterium is less easily abstracted than hydrogen, it might be expected that the deuterated antioxidant should evidence diminished effectiveness. On the other hand, the deuterium atom might be metered out more efficiently, and so permit the antioxidant to last longer. There may also be side reactions such as a hydrogen-deuterium exchange that can obscure the isotope effect, or direct oxidation of the antioxidant to initiate new chains. To sort out these various parameters, preparation of analogs of model antioxidants is being planned in which only the active hydrogen and/or all of the hydrogens are replaced by deuterium. The effect of these antioxidants on model esters and their deuterated analogs under various oxidation conditions will be ascertained. From the information obtained, the more significant parameters that affect these systems can probably be determined.

Other Aspects of the Deuterated Fluids Study

The surface properties and the surface reactivities of deuterated fluids on bearing metals and other materials will have a critical effect on their behavior as lubricants. These will be determined by surface tension and wettability measurements, and by use of Fourier Transform IR and other applicable instrumental techniques.

Finally, to bring into proper perspective the role of deuterated fluids in practical applications, the life-test of selected mechanisms lubricated with deuterated fluids or greases is being planned. Because of their present high cost, these lubricants will be used initially in systems requiring small amounts, such as guidance gyro minature bearings, actuating mechanisms, fan motors, etc. At a later date, it is planned that larger volumes of the fluids will be tested in critical high temperature applications, such as special purpose gas turbine engines.

Further information can be obtained from

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III. H-46 Helicopter Fiberglass Rotor Blades

As a result of major maintenance problems with the H-46 helicopter metal rotor blade (Fig. III-1), the Naval Air Systems Command initiated a contract with the Boeing Vertol Company in early 1975 to develop and produce a replacement composite rotor blade. Principal objective of the development program was to develop a composite blade which exhibited the same flying qualities and performance as the metal blade but with significantly improved reliability and maintainability.

The composite rotor blade, in cross section, has two structural configurations. The aft portion of the blade consists of a tapered Nomex honeycomb core and fiberglass crossply skins approximately 0.018" thick. These skins are made of +45° crossply broadgoods obtained as a prepreg with epoxy resin. The foreward portion is a D-spar made of a 0.25" thick composite consisting of +45° crossply fiberglass, 0° fiberglass, +19° crossply graphite, 0° fiberglass and +45° crossply fiberglass. E-glass is used for the skin structure and the spar. S-glass is used for fiberglass straps in the blade.

Flight testing began in May 1978 and was completed twelve months later. A total of 18,658 blade flight hours were accumulated with no returns to depot level required. The average hours per blade during this demonstration was 311 hours and the six high time blades had accumulated 778 hours each by the end of the test period.

The values for reliability and maintenance (R&M) parameters obtained during the reliability demonstration are shown in Table III-1.
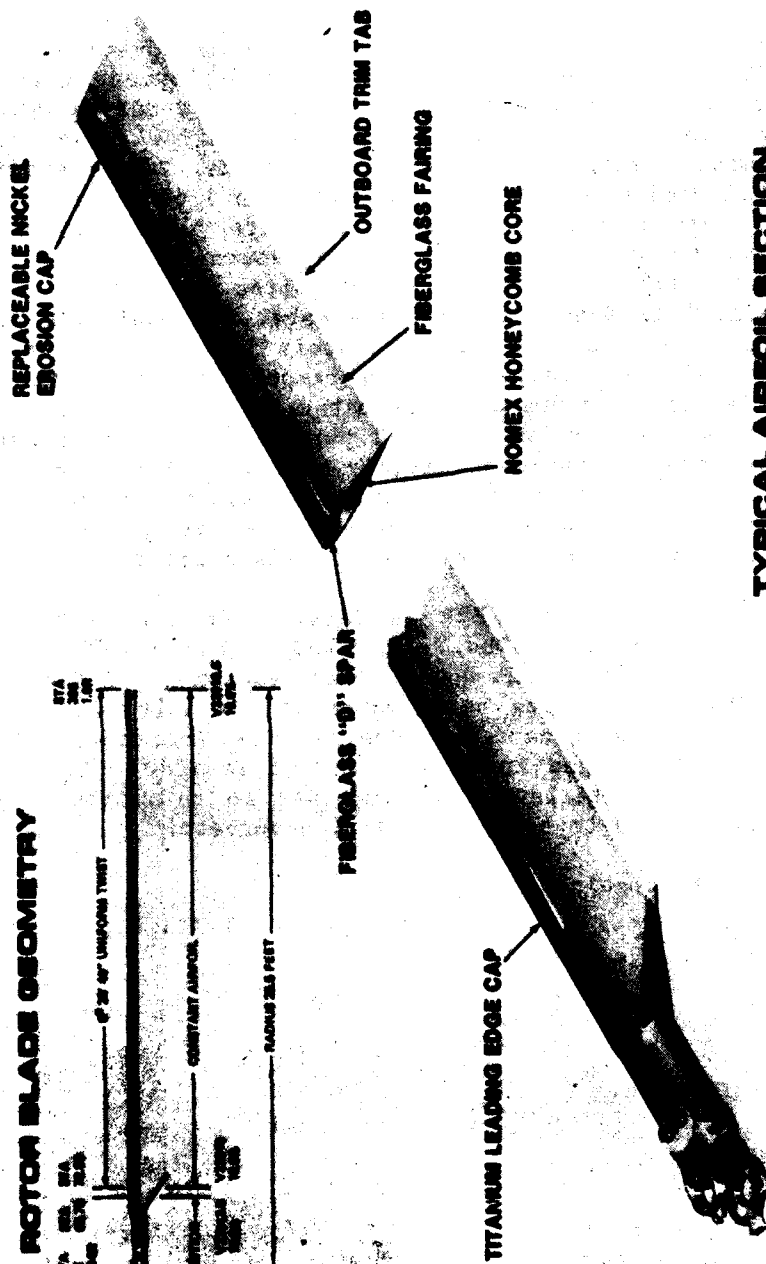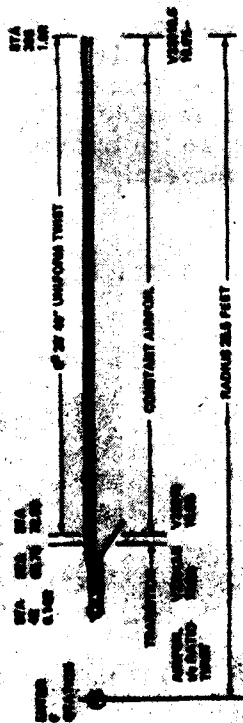
Table III-1 — Reliability demonstration for H-46 fiberglass rotor blades

	Metal Blades	Fiberglass Blades	
		Objectives	R&M Demo
MBFHBMA (1)	56 hrs.	56 hrs.	548 hrs.
MBFHBRD (2)	464	2500	No Removals
MBFHBF (3)	280	280	666

(1) Mean blade flight hours between maintenance actions
(2) Mean blade flight hours between removal to depot
(3) Mean blade flight hours between failures

The reliability demonstration clearly indicated that the H-46 fiberglass rotor blade met or exceeded all R&M goals and that the procedures, materials and ground support equipment were acceptable and functional for the repairs for which they were designed.

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REPLACEABLE NICKEL EROSION CAP

OUTBOARD TRIM TAB

FIBERGLASS FAIRING

NOMEX HONEYCOMB CORE

FIBERGLASS "D" SPAR

TITANIUM LEADING EDGE CAP

ROTOR BLADE GEOMETRY

TYPICAL AIRFOIL SECTION

NOMEX HONEYCOMB CORE

FIBERGLASS X-PLY SKINS

TRAILING EDGE WEDGE

GRAPHITE X-PLY

STIFFENER

FIBERGLASS D SPAR

TITANIUM LEADING EDGE

DEICE BLANKET

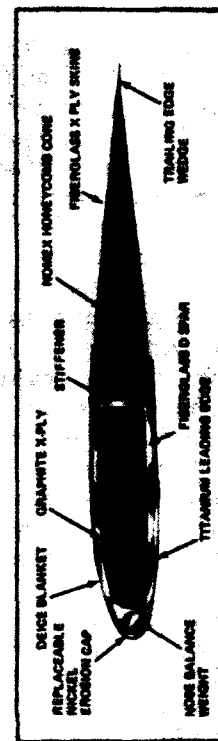REPLACEABLE NICKEL EROSION CAP

NOSE BALANCE WEIGHT

R-362

Fig. III-1 — CH-46 Fiberglass rotor blade

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Operational Experience

Production blade delivery began in March 1979. A Marine CH-46F squadron from New River, NC completed the first complete extended deployment with the production fiberglass rotor blade (FRB). In a five month period during which a total of 1507 flight hours were generated, one FRB was removed for cause and it subsequently was repaired aboard ship and returned to service. In a previous similar deployment with metal blades by the same squadron, in 1767 flying hours, a total of 78 metal blades were removed for cause; all were judged beyond the capability of repair by field maintenance and had to be returned to depot. The savings in transportation costs and additional spares required more than balances the cost of the labor generated in substituting blade sets. In addition, depot rework data for metal blades indicated that approximately 12-13% of all blades returned for depot rework must be scrapped. With respect to the first FRB deployment noted above, the group commander estimated that the operational availability of his aircraft had improved by 10 to 11 percent over their previous deployment, and he attributed that improvement largely to the reliability of the FRB. Whereas, with metal rotor blades about 14 minutes of every direct mainte-nance man-hour per flight hour is devoted to blade-related maintenance, this figure is reduced to less than a minute in the case of fiberglass rotor blades.

The most recent operational data for FRB is dated 1 January 1982. As of that date, 1,016 blades had been delivered. They had logged 291,000 flight hours and the high-time blade had 1810 flight hours. The resulting R & M data is presented in Table III-2. The outstanding performance of the fiberglass blade is demonstrated. The time between maintenance actions has been increased greatly and none of the blades have been damaged in service beyond repair. All of the repairs could be performed at the IMA level and none had to be returned to a depot. The FRB program is considered to be an unqualified success.

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Naval Air Systems Command
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Table III-2 — R & M Data for rotor blades

	COMPOSITE BLADES	METAL BLADES
MBFHBMA[1]	2000 hr.	135 hr.
MBFBRD[2]	None removed	1,142
Maintenance $\dfrac{\text{Man hr.}}{\text{Flight hr.}}$	0.13	0.96

(1) Mean blade flight hours between maintenance actions
(2) Mean blade flight hours between removal to depot

IV. Ion Implantation

Ion implantation consists of injecting selected elemental ion species beneath the surface of materials by means of a high-energy ion beam from an accelerator (usually at tens to hundreds of kilovolts). This injection process produces an intimate alloy of the implanted and host elements without producing the sharp interface that is characteristic of most coatings and hence avoids the related adhesion problems. The resultant depth distribution and alloy composition depend on the energy and atomic number of the projectile as well as on the atomic number of the host. Typically, penetrations of 0.01 to 1.0 microns are achievable with concentrations of up to 50 at%. The implanted dose (i.e. impurity as measured in atoms per unit volume) is obtained from the ion beam charge, the implanted target area, and the implanted species depth distribution.

Ion implantation is not a thermodynamical equilibrium process. Metastable alloys can be formed without regard for the conventional considerations of solid solubility and diffusivity. Any elemental species can be implanted into any other material. Heating of the implanted alloy to sufficiently high temperatures will, of course, ensure equilibrium conditions, but several durable metastable (or amorphous) phases with potentially interesting physical properties have been formed by implantation. Table IV-1 lists many of the ion beam parameters, along with typical ranges of values that pertain to ion implantation for materials modification. The ability to control and reproduce these ion beam parameters is especially important for large scale commercial usage.

Table IV-1 — Ion implantation parameters

Implanted Elements	– Virtually any element from hydrogen to uranium can be implanted.
Ion Energies	– Normally 2 TO 200 KeV. Energies up to 5 MeV may be obtained with the Van De Graaff Accelerator.
Ion Ranges	– Vary with ion energy, ion species and host material ranges normally 0.01 m to 1.0 m.
Range Distribution	– Approximately Gaussian, choice of energies allow tailored depth distribution profiles.
Concentration	– From trace amounts up to 50% or more.
Host Material	– Any solid material can be implanted.
Special Effects	– Sputtering, radiation damage, radiation

Ion Implantation - Advantages and Limitations of Technique

Some of the advantages and limitations of ion implantation in comparison to other surface treatments (such as coatings) are listed in the Table IV-2. A basic limitation of ion implantation is that as a line-of-sight process, it is not feasible to apply it to samples having complicated reentrant surfaces. The shallow depth penetration would seemingly limit the technique for engineering applications; however, there are several situations involving both physical and chemical properties which are extremely surface sensitive as well as conditions under which the effect of the implanted ions persists to depths far greater than the initial implantation range.

As for the advantages, the fact that ion implantation is a non-equilibrium technique permits the formation of surface alloys whose formation is independent of solubility limits and diffusivities governing conventional alloy formation. This will be demonstrated later by the formation of unique metastable amorphous surface alloys for bearings.

Table IV-2 — Advantages and limitations of ion implantation

Advantages	Limitations
(1) Solid solubility limit can be exceeded	(1) Line-of-sight process
(2) Alloy preparation independent of diffusion constants	(2) Shallow penetration
(3) Allows fast screening of the effects of changes in alloy composition	(3) Relatively expensive equipment and processing costs
(4) No sacrifice of bulk properties	
(5) Low temperature process	
(6) No significant dimensional changes	
(7) No adhesion problems since there is no sharp interface	
(8) Depth concentration distribution controllable	
(9) Clean vacuum process	
(10) Highly controllable and reproducible	

A. Improving Corrosion Resistance of Bearings By Ion Implantation

Because of the utility of the ion implantation process, scientists have examined and developed Navy applications of ion implantation to enhance life cycle duration, reduce maintenance, and increase reliability of Navy systems.

One such application is the ion implantation of aircraft bearings to improve corrosion resistance. Corrosion is one of the most common reasons for rejection of bearings during periodic scheduled overhaul in the U. S. Navy. Corrosion also causes premature (catastrophic) inservice failures and unacceptably short shelf-lifetimes of new or unused bearings. For example, the majority of bearings reconditioned at the U. S. Naval Air Rework Facilities are unused spares that have corroded on the shelf, rather than those recovered after use in aircraft engines. It is estimated that the Navy spends more than a million dollars ($1M) per year for the replacement and reconditioning of turbojet mainshaft engine bearings alone, excluding labor costs. Turbojet engines that are used only intermittently exhibit the worst corrosion problems, consisting of local corrosion pits formed at the contact points between the rollers or balls and the inner or outer race. These pits act as initiation sites for catastrophic fatigue failures.

Responding to these problems, NRL established a research program to investigate the application of ion implantation to produce corrosion resistant bearings made of 52100 and M50 steel, which are two of the most commonly used alloys for Navy equipment. The research program included the development of implantation treatments and subsequent corrosion tests of the bearings under field service conditions. Quantitative electrochemical testing of the bearings were conducted to measure the corrosion kinetics and resistance to localized corrosion (pitting) in the contaminating marine environment to which Navy equipment is generally exposed. In addition, the mechanical stability of the implanted surfaces was measured to determine if the implantation process degrades the rolling contact fatigue lifetime of the bearings.

The implantation energies and ion fluences used in the anti-corrosion implantation treatments were chosen to produce a 15 to 30 atomic percent concentration of the implanted elements in a region extending from the surface to a depth of about 80 nanometers. The choice of ions is determined primarily by the known anti-corrosion behavior of the ions in bulk materials. Some examples of the behavior include the corrosion-resistance of stainless steel by the addition of chromium, improved pitting resistance in steels by addition of molybdenum, formation of a stable corrosion resistant oxide by the addition of titanium, and the stabilization of an amorphous corrosion resistant phase by phosphorus when suitably quench-alloyed with iron.

Figure IV-1 shows the pitting corrosion test geometry used to simulate the field service conditions for both AISI 52100 and M-50 high temperature turbojet engine bearing alloys. Figure IV-2 shows the flat surface (simulating the race) of an M50 test sample after testing for the unimplanted and Cr-implanted conditions and it demonstrates the significantly higher corrosion resistance of the implanted surface.

1. Test pieces (both M50 alloy steel) were placed in contact as indicated by the dotted line.

FLAT SURFACE
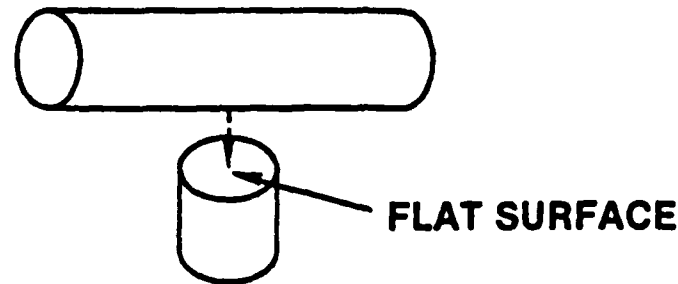
2. Both pieces in place were immersed in chloride-contaminated oil for 2 hrs., removed, and allowed to dry.

3. A meniscus of contaminated oil was retained between the two parts:

UPPER CYLINDER (end view)

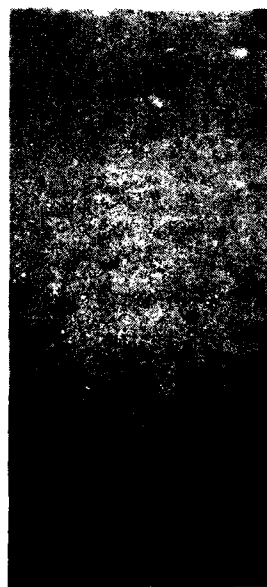Cl-CONTAMINATED OIL

FLAT SURFACE
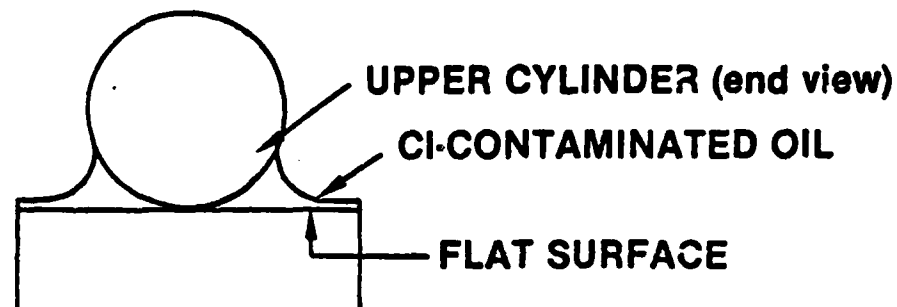
4. The above arrangement was exposed to moist air cycled between 4° AND 40°C for 2 weeks.

Fig. IV-1 — Laboratory-simulated field service test of corrosion of bearings

UNIMPLANTED　　　　　R-366　　　　**Cr-IMPLANTED**

Fig. IV-2 — Photomicrographs of AISI-M50 steel disk samples after a corrosion test. A cylinder of M50 steel lay on the disk for 4 weeks at temperatures from 4°C to 40°C with salt-contaminated oil between them.

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Tests in chloride ion solutions were performed to measure the resistance of the ion implanted surface alloy to localized pitting corrosion. These tests were conducted in a pH6 buffered, 0.1 molar salt (NaCl) solution. Figure IV-3 presents potentiodynamic polarization scans for the 0.1M NaCl solution for tantalum implants in the 52100 alloy. The pertinent characteristic of each curve is the breakdown potential, E_b, which characterizes the metal's ability to withstand pitting attack (i.e., higher E_b indicates better protection). The breakdown potential is that voltage on the curve where there is a sudden increase in current density. Note the large improvement in E_b following Ta implantation.

In addition to these corrosion tests, twenty bearings of the H-46 helicopter turbojet engine have been implanted with the most promising species, ten with Cr and ten with Cr + P. The Cr + P implantation promotes the formation of an amorphous surface alloy that apparently provides superior protection for splat-quenched alloys. (The Cr + Mo combination is also being implanted in present laboratory investigations for its corrosion-resistant qualities). Results of fatigue endurance tests were compared with those of a set of ten unimplanted bearings, which provided a baseline or control group. No significant differences in fatigue endurance appeared between the two groups. Two T-63 helicopter Gas Turbine Engine Bearings have passed similar endurance tests after implantation with Cr + P. These findings demonstrate that the ion implantation process does not degrade mechanical performance of the bearings. Implanted jet aircraft and helicopter engine bearings have now passed engine performance test up to 400 hrs. at conditions simulating the speeds, loads, and temperatures experienced by engines in operational use.

In addition, twelve H-46 helicopter hinge pin bearings for rotor blade support have been implanted with Cr and Cr + P and delivered to the NARF - North Island for installation and field service tests over the next two years. Similarly, ten T-58 engine bearings from the H-46 helicopter and ten J-79 mainshaft engine bearings from F4's have also been implanted (one half with Cr, one half with Cr + P) for field evaluation.

These programs have demonstrated that ion implantation improves the corrosion resistance of 52100 and M50 bearings without degrading mechanical performance. They have also suggested that production line implantation of bearings could be feasible.

B. Palladium Implanted Titanium

The Navy is also interested in ion implantation as applied to non-aqueous corrosion resistance. The system chosen for initial study in the Naval Research Laboratory program was palladium (Pd) implanted into titanium (Ti). This was selected because it is well known that small additions of Pd in bulk alloys (0.1 at%) produce a dramatic reduction in the corrosion rate of titanium in hot, concentrated acids.

In this study samples of pure titanium rod (3/8 inch diam.) were mounted in epoxy molds and polished to a mirror finish. These surfaces were implanted with palladium to a fluence of 1×10^{16} ions/cm^2 at an energy of 90 Kev. The resulting palladium concentration profile was approximately gaussian shaped and centered at a depth of 240 angstroms beneath the titanium surface. The concentration of palladium at that depth was 5 at%, with less than 0.1 at% Pd at the titanium surface.
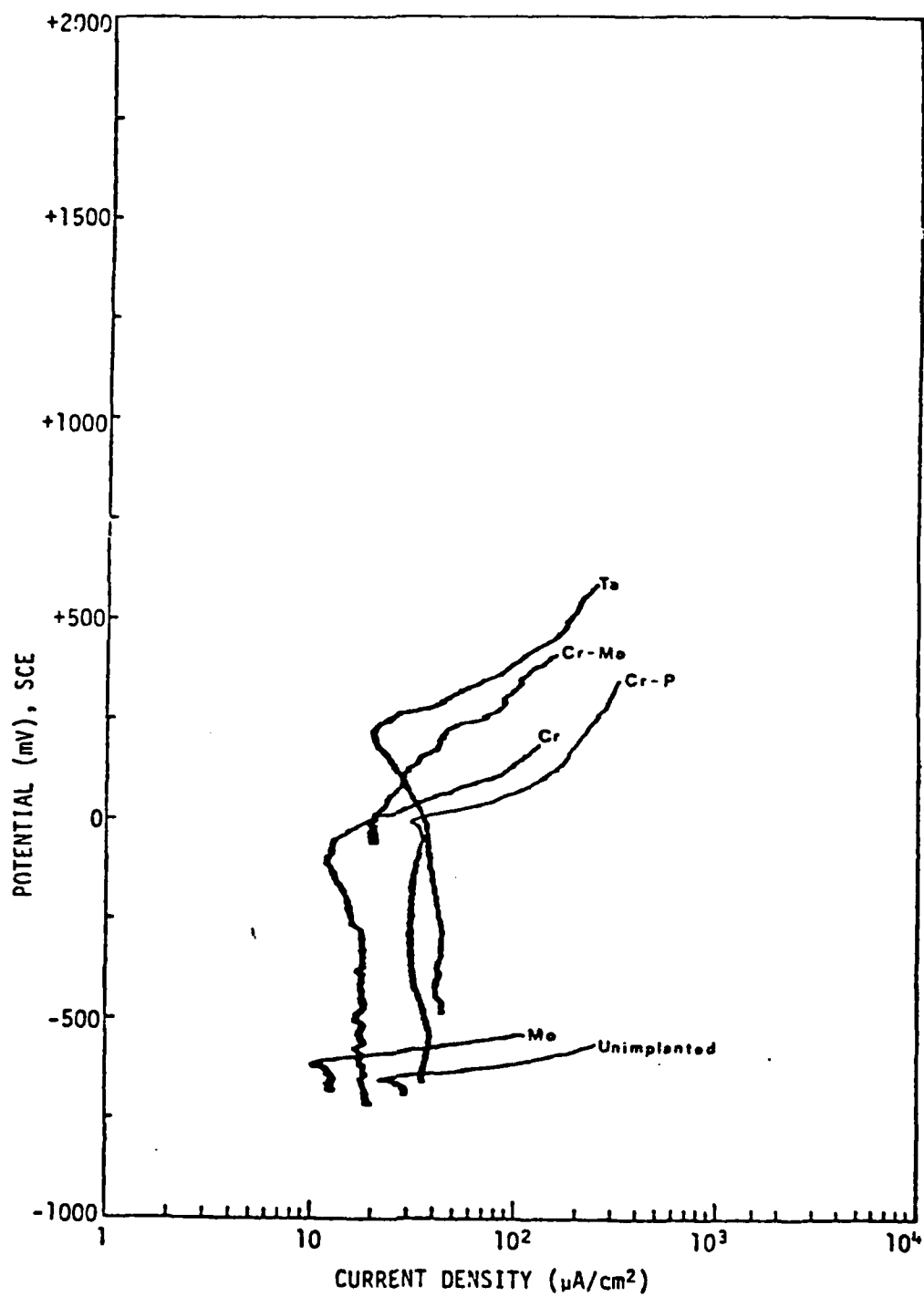
Fig. IV-3 — Anodic polarization curves of implanted 52100 bearing steel in 0.01 M NaCl solution buffered at pH 6 with cathodic pretreatment

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Figure IV-4 shows electrode potentials vs. Hg/Hg_2SO_4 as a function of immersion time for pure Ti, pure Pd, and Pd-implanted Ti samples in boiling 1M H_2SO_4. The steady-state corrosion potential of the implanted sample is much closer to that of pure palladium than that of pure titanium. Moreover, in the first few minutes of immersion, the implanted samples showed a rapid shift from an electrode potential near that of pure Ti to a potential close to that for pure Pd. After 1 minute in the case of two of the implanted samples and after 1.5 minutes for a third, the electrode potential was -1.0 volts vs. Hg/Hg_2SO_4 and tending toward the potential of pure titanium. During the next few seconds in each case, however, the electrode potential reversed toward the Pd direction as the Ti-rich surface dissolved away to expose a new surface region containing an increased concentration of Pd.

The buildup of palladium at the surface during the corrosion process was determined by Rutherford backscattering of helium ions, and is shown in Fig. IV-5. The increased peak height in the Pd profile with time indicates that Pd is being built up at the surface. The area under the curves, which is proportional to the total amount of Pd retained in the sample, is the same for all three curves indicating that no Pd is lost during the corrosion process. The maximum surface concentration of Pd built up during this process was about 20 percent. In the longest experiment run to date, Pd was retained for as long as 8 hrs.

Figure IV-6 shows potentiostatic anodic polarization curves for pure titanium, pure palladium, and palladium-implanted titanium in boiling 1M H_2SO_4. All curves were determined after steady-state open circuit potentials were first established (2 to 2-1/2 hrs. immersion). The anodic curve for pure titanium shows the normal active-passive behavior which has been typically observed. Well defined Tafel slopes were not observed in the active region, but the corrosion rate at the open-circuit potential was determined by colorimetric analysis of the solution to be 3.7 mA/cm^2, on the basis that the overall anodic reaction is $Ti \longrightarrow Ti^{+3} + 3e^-$. The implanted samples display a passive current density of 2 to 6 $\mu A/cm^2$, which may be defined as the corrosion rate at the open-circuit potential. Thus, implantation with Pd lowers the corrosion rate of Ti by a factor of about 1,000.

To summarize, ion implantation of titanium with palladium reduces the open-circuit corrosion rate in boiling 1 M sulfuric acid by a factor of about 1,000. The open-circuit corrosion potential is shifted approximately 0.9 volts in the Pd direction and is a mixed potential between pure titanium and pure palladium. Electrochemical measurements and Rutherford backscattering analysis indicate that the improvement is due to the initial preferential dissolution of titanium and the retention and buildup of implanted palladium. However, the improvement observed suggest that Pd-implanted Ti could be applied in problem areas such as crevices where local acidity leads to corrosion.

C. The Effect of Ion Implantation on Fatigue Life in Ti-6Al-4V

Substantial improvement in corrosion and wear resistance has been demonstrated in various ion implanted metals and alloys. Recent Navy studies have shown the potential value of ion implantation in the extension of fatigue life.
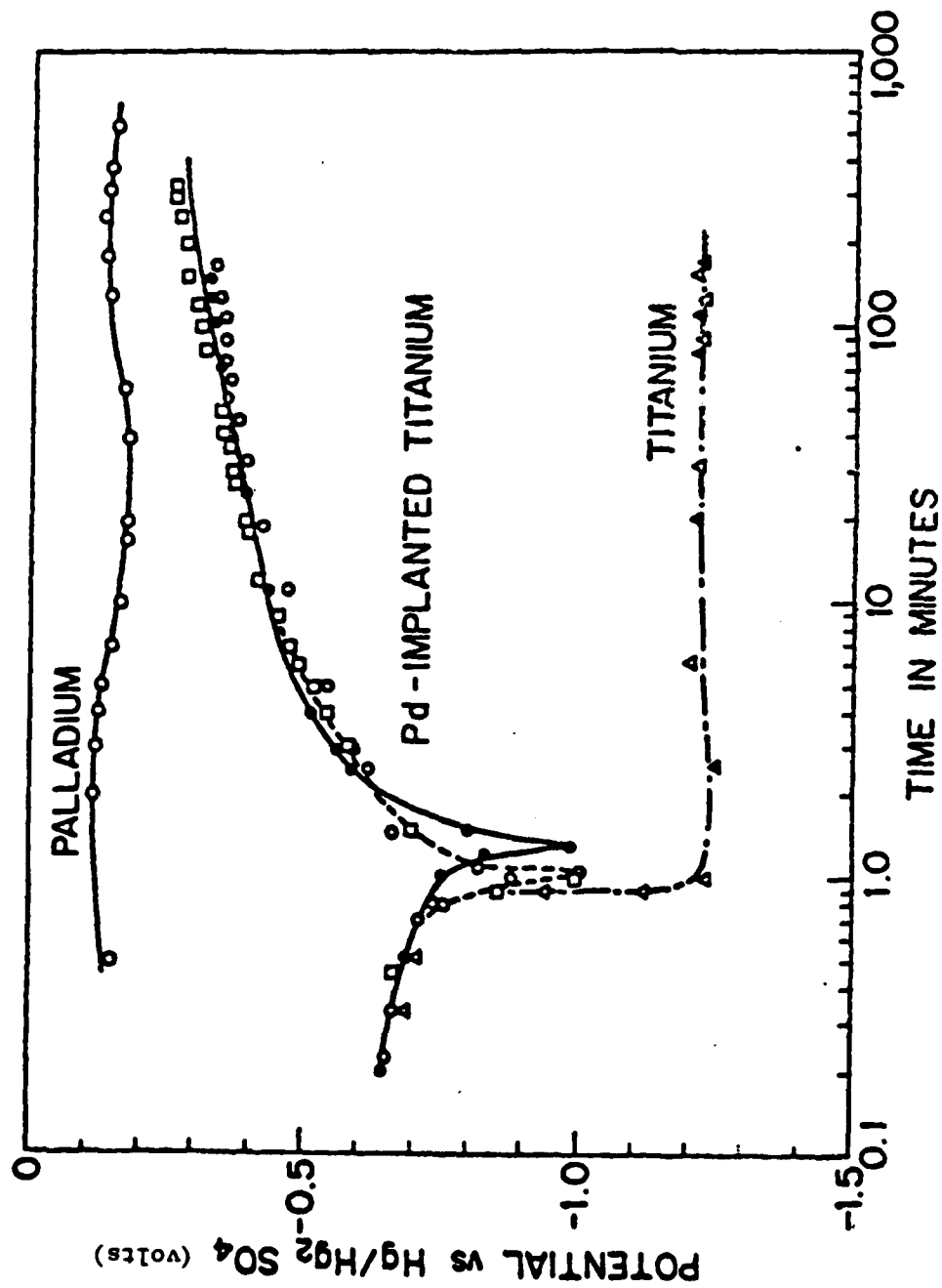
Fig. IV-4 — Open circuit corrosion potentials as a function of immersion time in boiling 1M H_2SO_4 for pure titanium, pure palladium, and palladium-implanted titanium
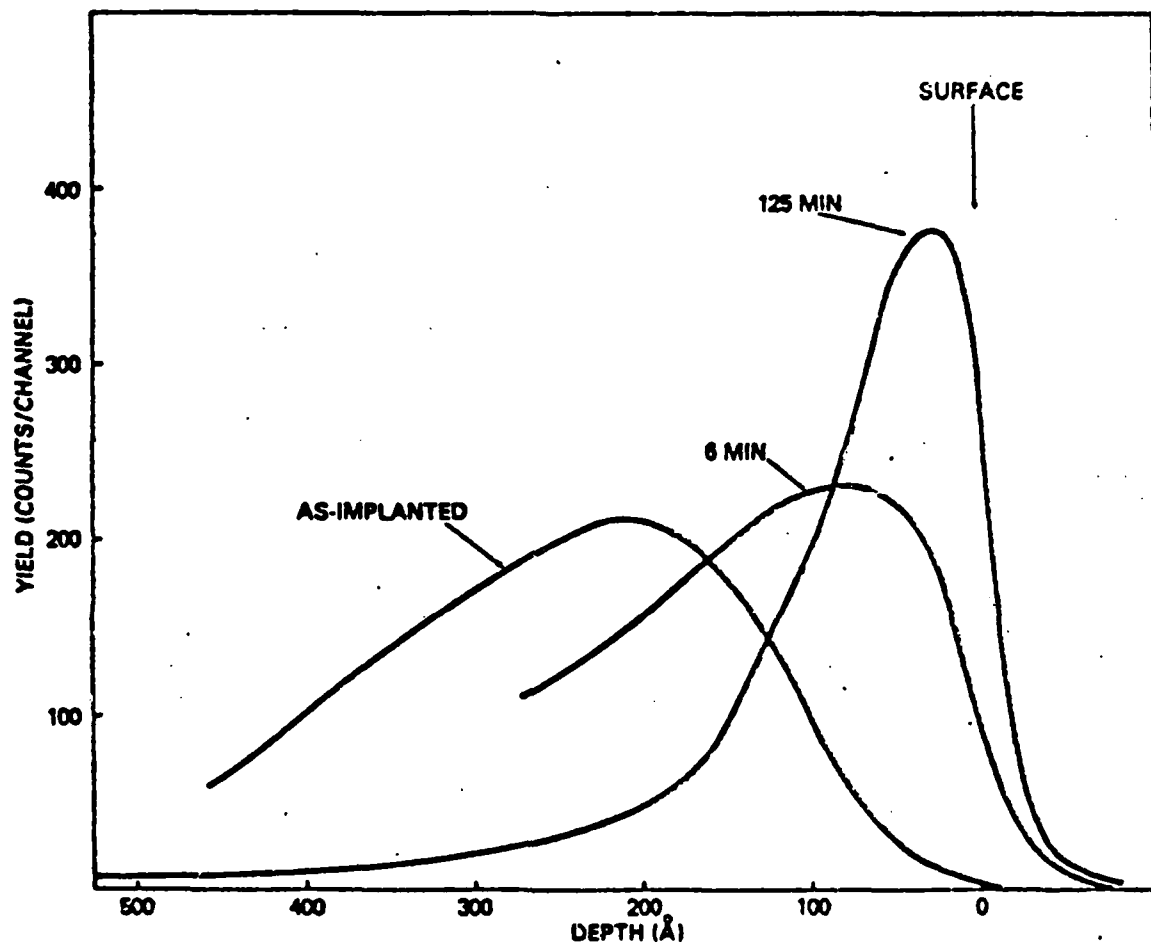
24

Fig. IV-5 — The energy spectrum of helium ions backscattered from ion-implanted Pd in pure Ti for an implanted sample and after two different immersion times in boiling 1M H_2SO_4
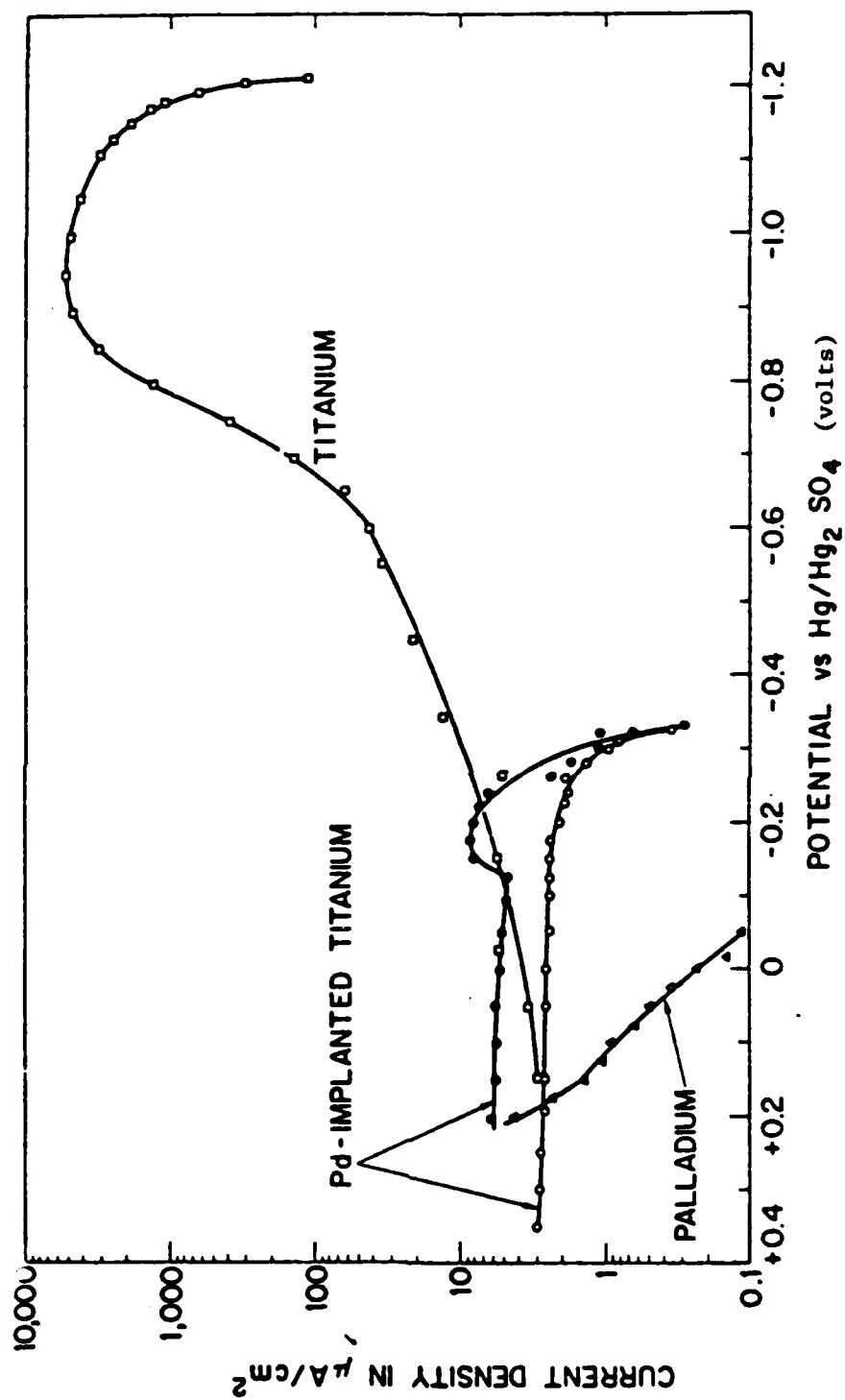
25

Fig. IV-6 — Anodic polarization curves for titanium, palladium, and palladium-implanted titanium in boiling 1M H_2SO_4

This work was undertaken to examine the influence of ion implantation on the surface microstructure and fatigue life of a technologically important alloy, Ti-6Al-4V. This alloy was chosen because of its widespread use in aircraft and the cost and performance benefits of improving its fatigue properties.

Carbon and nitrogen were used as the implanted species because these have proved most effective in earlier mechanical property studies. The rotating beam test was used to determine fatigue lifetime. Samples were characterized by a variety of methods, including Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Nuclear Reaction Analysis (NRA). The results show a substantial improvement in fatigue life, particularly for the carbon implant.

Nitrogen was implanted as N_2^+ at 150 KeV, or 75 KeV per atom. Carbon likewise was implanted at 75 KeV. Temperature of the fatigue samples during implantation was estimated not to exceed 100°C. The total dose for both species was 2×10^{17} at/cm^2, except where otherwise noted. The concentration profiles of the implanted nitrogen and carbon were measured by NRA.

Rotating beam samples were used for fatigue testing, with a gage length of 1 in. and a minimum diameter of 0.25 in. Testing was done at approximately 30 Hz. Preliminary fatigue tests on electro-polished samples gave anomalously short lifetimes, so mechanically polished surfaces were used in all tests reported here. A 400 grit finish, with all radial scratches carefully eliminated, was chosen as satisfactory. No increase in fatigue life can be expected for a more finely polished surface finish.

The fracture surfaces of the fatigue samples were examined by SEM with particular attention to the origination point of the fatigue crack. By following surface striations it was usually not difficult to distinguish between surface and subsurface crack origination. Subsurface origin points could be determined to within about 25 m or less.

Results of the fatigue life measurements are shown in Fig. IV-7. The unimplanted endurance limit of 73 ksi is increased approximately 10% by nitrogen implantation and 20% by carbon implantation. At stresses above 100 ksi the unimplanted lifetimes decrease sharply. The effect of nitrogen implantation nearly disappears at these stress levels while carbon implantation maintains a factor of 4 to 5 increase in lifetime even at the highest stresses measured.

It has been reported that subsurface fatigue crack origins can occur in titanium alloys even in the absence of inclusions or other common stress concentrators. The subsurface origin does not appear to affect the fatigue lifetime, and occurs mainly in the longer lifetime tests. Subsurface crack origins occur in nearly all samples with a lifetime greater than 10^5 cycles, whether implanted or not, while those with a lifetime less than 10^5 cycles typically show
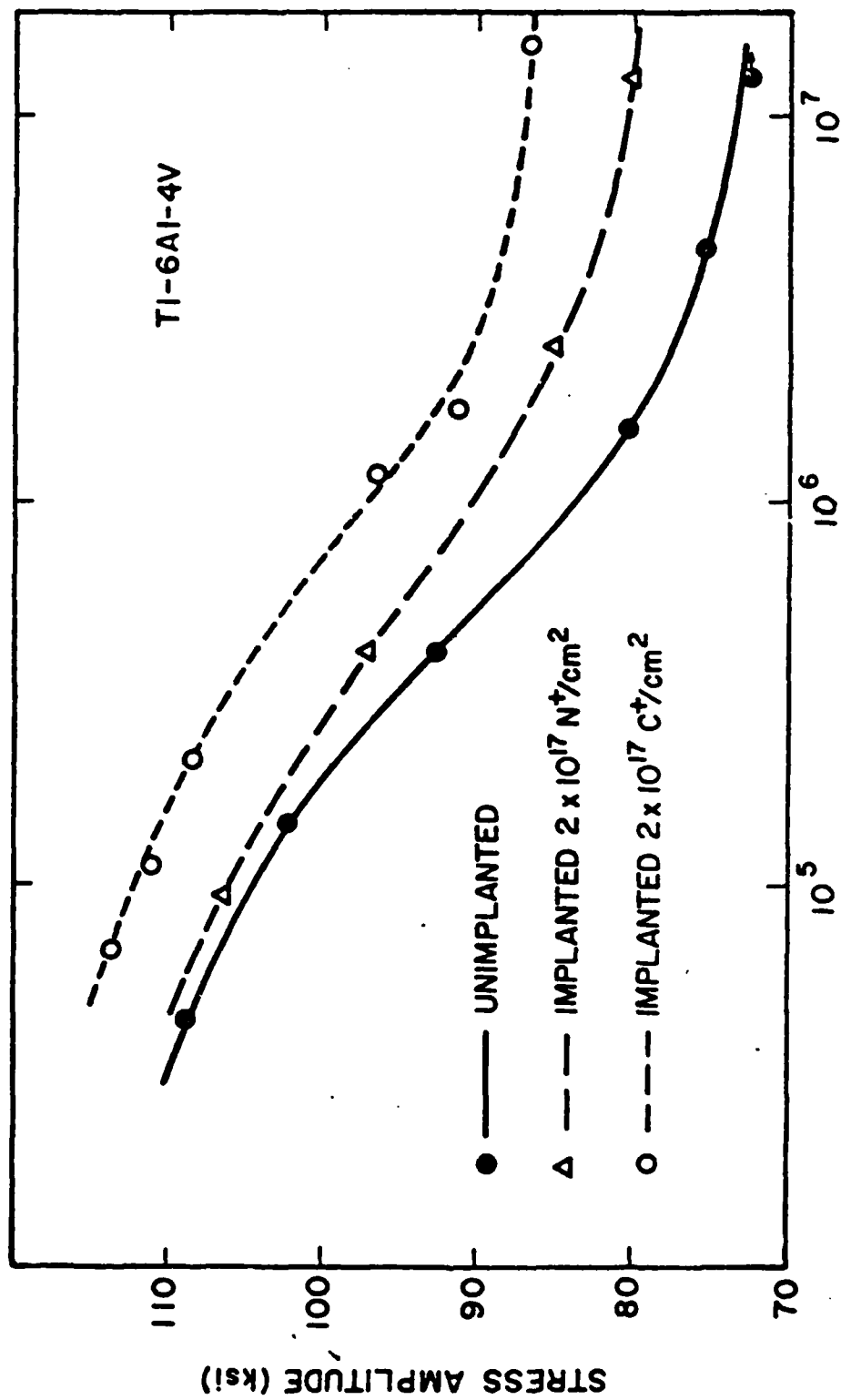
CYCLES TO FAILURE

Fig. IV-7 — Maximum stress vs. cycles to failure for mill annealed Ti-6Al-4V in conditions indicated. Rotating beam fatigue.

a surface origination. The subsurface origin points ranged in depth from 25 to 150 μm. In a few samples the origin was difficult to identify accurately, and some of these may be subsurface origin points at less than 25 μm depth.

It is perhaps surprising that an altered layer only a few tenths of a micron thick can have such a large influence on fatigue life. The original expectation was that implantation would benefit fatigue life by creating a compressive stress, and by inhibiting the development of slip steps on the surface which could open into cracks. However, the extensive occurrence of fatigue crack origins at depths far below the implanted layer indicates a more complex interaction between the implanted layer and the fatigue process in the bulk. Obviously the effect of implantation goes beyond the introduction of a compressively stressed surface layer.

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V. Protection of Gas Turbine Blades Against Hot Corrosion

Gas turbines are being adopted by the U. S. Navy for ship propulsion, with 80 turbine-powered vessels (30 DD-963 class destroyers and 50 FFG-7 class guided missile frigates) soon to be in the Fleet. These gas turbines are subjected to sea salt ingestion, high sulfur (up to 1%) fuel, and broad engine temperature operating ranges. This exposure can cause rapid corrosion and failure of unprotected engines constructed of aviation-type alloys. The Navy therefore must seek new technology to enable shipboard turbines to resist the aggressive marine environment.

Engine air filtration provides the first line of defense but can not be relied on solely, because (1) total salt removal is not achieved, and (2) battle damage could destroy the filtration system. Nor is it possible, for economic and tactical reasons, to insure a supply of low sulfur fuel. The most critical problem with gas turbines at sea is "hot corrosion" - an accelerated, high-temperature corrosion caused by the reaction of sea salt with the hot turbine blades. Previous theory held that this hot corrosion was caused by deposition of molten Na_2SO_4 from sea salt on the blade surface, and would be aggressive only when blade temperatures were sufficiently high that the Na_2SO_4 (M_p 884°C) would remain molten. Sodium chloride and by-product sulfide phases may have effects, but these were considered to be only secondary. Unexpectedly, however, severe hot corrosion of blades was discovered to have occurred at only 650° to 750°C during low-power tests of the Navy ship propulsion engine (LM-2500) on the GTS CALLAHAN. This discovery caused serious concern because the LM-2500 engine will operate most of the time at low or intermediate power levels.

Blades of the LM-2500 are protected by a thin coating of an alloy of cobalt, chromium, aluminum, and yttrium (CoCrAlY) developed specifically to resist hot corrosion. This coating was quite effective in high-power (900°C blade temperatures) engine tests which ran as long as 7000 h. In low-power operation, however, characteristic pitting (Figure V-1) routinely penetrated the CoCrAlY in less than 3000 h (within 500 h in one sea test).

A NAVSEA-NRL Hot Corrosion Task involving cooperative industry-NRL research was established to solve the hot corrosion problem. This Task was the first to explain the second region of hot-corrosion susceptibility at 650° to 750°C, heretofore unrecognized by the gas turbine industry. This lower temperature hot corrosion is caused by formation of low-melting mixed sulfates from the cobalt sulfate-sodium sulfate (eutectic at 575°C) and nickel sulfate-sodium sulfate (eutectic at 670°C) systems. Cobalt and nickel sulfate are thermally unstable and undergo a reversible decomposition to the respective metal oxide and SO_3 at elevated temperatures:

$$MSO_4 \longrightarrow MO + SO_3 \qquad (M = Co \text{ or } Ni).$$
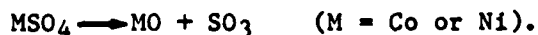
However, at 650° to 750°C, the equilibrium partial pressure of SO_3 is low; as little as 10 to 100 Pa of SO_3 is enough to reverse the reaction. These levels of SO_3 are readily attainable by oxidation of the up to 1% sulfur allowed in Navy fuel. Therefore, cobalt and nickel sulfate are formed by reaction of the

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Fig. V-1 — Pitting of LM-2500 turbine blade after 3,000 hrs of low-power operation

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oxides normally occurring on the blade surface with SO_3 in the engine gas. These sulfates interact with Na_2SO_4 from the sea salt to produce a mixed sulfate film, which is both molten and, because of the metastability of the metal sulfate, acidic (rich in SO_3). The combination causes severe corrosion, normally in the form of a characteristic pitting.

NRL research has been fundamental in elucidating the low-temperature corrosion mechanism. In the early stages of the problem, NRL experiments showed that the decomposition of mixed sulfate deposits produced corrosion identical to that seen in low-power engine tests. Later NRL work demonstrated that the mixed sulfates are produced from the metal oxides and Na_2SO_4 under the very low SO_3 pressures indicated, and that the total process of eutectic sulfate formation and corrosion could in fact be duplicated in the laboratory.

The clear identification of the existence and mechanisms of low-temperature hot corrosion, including the critical role of SO_3 and the susceptibility of cobalt-based and, to a lesser extent, nickel-based alloys, has provided the basis for NAVSEA to initiate the development of improved coatings and blade alloys to protect the fleet's turbines against both low- and high-temperature hot corrosion.

As part of this program, under Navy contract, Pratt and Whitney is developing two advanced coatings as potential replacements for the currently used BC21 CoCrAlY coatings. One of these is also CoCrAlY with a chromium content of approximately 30%, versus the nominal 22% content of the BC21. The second one is a silicon overlayer on CoCrAlY in which the silicon is applied by physical vapor deposition. Laboratory burner rig tests indicate that the advanced coatings provide a 4x improvement in low temperature corrosion resistance with only nominal decrease in high temperature corrosion resistance. The next step will be to conduct sea tests to verify the results of the laboratory tests.

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VI. LIFE ENHANCEMENT OF NAVAL VESSELS

The Naval Sea Systems Command (NAVSEA) has an active program on life enhancement of naval vessels through such means as improved coatings for corrosion control and advanced materials with improved fatigue and toughness properties and increased corrosion resistance. Examples are discussed below together with some of their characteristics.

PLASMA SPRAYED COATINGS FOR NAVAL MACHINERY COMPONENTS

Thermal spray coating techniques are being employed for a large number of applications in the U. S. Navy, and interest in their utilization is growing. In particular, there is great interest in the plasma spray process (PSP) because it provides a denser and more adherent coating than can be produced with other conventional thermal spraying methods. An investigation was conducted of PSP for potential naval machinery and structural applications in the marine environment.

Engineering properties of representative plasma sprayed metal, ceramic and metal/ceramic composite coatings were determined, including salt-water corrosion resistance, relative abrasion wear resistance and the effect of the process on substrate alloy fatigue strength. The results are summarized below.

A. Corrosion

Five different plasma sprayed coatings were exposed for one year in three different environments, i.e., marine atmosphere, tidal waters, and constant flowing seawater. The coating materials were Al_2O_3, 87% Al_2O_3 - 13%TiO_2, Inconel 625, WC in Co matrix, and aluminum bronze. Wire flame sprayed Al was used as a standard for comparison. Coatings of 5, 10, 15, and 20 mils thickness were sprayed onto a mild steel substrate. Results after one year of exposure indicated that the aluminum coating was the superior corrosion resistant material in the marine atmosphere. The ceramic materials showed a tendency for cracking and spallation in the marine atmosphere. However, for the two submersion environments, both plasma-sprayed ceramic materials displayed excellent results in all coating thicknesses with no apparent corrosion. The Al coating performed moderately well in these two environments but the other three materials (Inconel 625, WC in Co, and Al-bronze) performed poorly. For tidal immersion tests, the $Al_2O_3-TiO_2$ material exhibited less biological fouling than the other materials. In general, coating performance improved with increasing coating thickness.

B. Fatigue

The effect of the plasma-spray coating process on the fatigue strength of class II shaft steel and monel K-500 was assessed. A ceramic (87%Al_2O_3-13%TiO_2) and a metallic (89.5%Ni-5%Mo-5.5%Al) were used to coat fatigue test specimens of both substrate alloys. These tests indicated that there was no reduction in fatigue strength of the two substrate alloys as a result of the extrinsic effects of plasma-spraying. Plasma-sprayed coatings, however, do not contribute to the fatigue strength of the the substrate material.

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C. Wear

A comparative analysis of the relative abrasive wear resistance of several plasma sprayed coatings was performed. Coated specimens were abraded against like material under a constant load for a given number of cycles with no lubricant. The volume of material lost during testing was used as the measure of abrasive wear resistance. WC in Co matrix was the most wear-resistant of the materials tested followed closely by Cr_2O_3 and WC in Ni matrix. The metal alloy coatings generally did not perform as well as the composites or the ceramics.

FLAME-SPRAYED ALUMINUM COATINGS

Another thermal spray process being evaluated for corrosion control is flame spraying of aluminum wire. The coating was applied in a Naval shipyard production environment to a broad range of propulsion plane valves. For a test group of approximately 360 valves coated and reinstalled aboard a ship, no deterioration of the spray coating was observed through two years of service. Similar valves painted with a conventional heat resistant aluminum paint and operating in the same environment and over the same period of time were repainted several times. Flame-sprayed valves were repacked with no detriment to the aluminized coating.

PROPERTIES OF ALUMINUM - MAGNESIUM ALLOY

The Naval Sea Systems Command initiated an alloy development program at the Aluminum Corporation of America. The goal is to provide a weldable aluminum alloy for marine applications with a minimum as-welded tensile yield strength of 30 Ksi (207 MPa) and with corrosion, fatigue strength, and fracture toughness properties at least equivalent to 5456 in the H116 or H117 tempers. The resulting developmental alloy was designated CS19 and used in a hot rolled and stretched temper of H3E19.

A characterization of the mechanical, toughness, and fatigue properties of a production heat and weldments of CS19-H3E19 aluminum-magnesium alloy was conducted. The alloy demonstrated higher yield and tensile strengths than 5456-H116/H117, and the as-welded yield strength approached the program goal of 30,000 pounds per square inch. The impact and fracture toughness as well as the fatigue and corrosion fatigue crack initiation and crack growth behavior of the alloy and its weldments were equivalent to those of the 5456 alloy. Sensitization of the alloy to simulate long-term natural aging did not significantly affect the mechanical, toughness, and fatigue properties. A study of the effect of welding heat input on the heat affected zone microstructure was undertaken since stress-corrosion cracking in the heat affected zone of sensitized, welded, thin CS19 plate occurred. The results indicated that control of welding parameters to achieve very low heat input may not be a fruitful approach for reducing stress-corrosion cracking susceptibility in CS19-H3E19, 1/4-in.-thick welded and sensitized plate.

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VII. Modification of Metal Surfaces By Laser Processing

The high power densities attainable with laser beams have made possible the development of a wide range of processing techniques which can improve the corrosion and wear resistance of metal surfaces. Table VII-1 lists most of these processes that use high energy lasers for surface modification. Some of these techniques are adaptations of methods that are currently popular in industry, while others were made possible only recently by the rapid heating and cooling rates attainable with high-power lasers.

TABLE VII - 1

TECHNIQUES FOR MODIFYING METAL SURFACE

BY LASER PROCESSING

- Transformation hardening

- Laser glazing

- Laser cladding

- Surface alloying

- Consolidation of coatings

- Laser melt/particle injection

Transformation hardening is typical of those techniques which are adapted from earlier practice. It utilizes the laser beam to rapidly heat the surface of a steel sample to austenitizing temperatures, permitting conduction cooling by the unheated base metal to quench the heated zone and produce a hard, martensitic structure on the surface. The advantages which accrue from using laser (or electron-beam) heating rather than induction or flame heating are that the minimal heating of the bulk material can prevent thermal degradation of bulk metal and can limit distortion of the part during quenching.

Laser glazing, which was developed at the United Technologies Research Center under funding from the Office of Naval Research and the Defense Advanced Research Projects Agency, differs from transformation hardening in that the surface layer is melted, not simply cycled through a set of solid-state phase transformations. The melting and rapid resolidification makes possible surface hardening, through the refinement of microstructure, of a wide range of alloy types. It can, in some alloys, improve the corrosion resistance by eliminating or minimizing phase separation and hence the nucleation sites for corrosion. Surface alloying, to be discussed in detail subsequently, can improve both the corrosion and wear-resistance of a wide range of alloy types. It does so by introducing alloying elements which improve the corrosion resistance or which stabilize hard, wear-resisting phases.

Laser cladding, a process developed at AVCO-Everett, is similar to traditional weld-cladding processes in that it uses the energy of the laser beam to fuse a metallic overlayer and weld it to the surface of the base metal. The material to be clad to the surface can be in the form of a loosely adhering

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powder or it can be wire that's fed directly into the weld pool. The consolidation of coatings with lasers differs from laser cladding only in the means of applying the cladding material prior to laser melting. The coating is previously applied by one of a number of processes such as flame spraying or plasma spraying and then laser-remelted to remove residual porosity as well as to improve its adherence to the base metal. These two processes are both suited for producing corrosion and wear-resisting surfaces and are the preferred techniques for several applications. In principle, the ease of applying diverse coatings by the thermal-spray processes together with the improved properties attainable with laser remelting should recommend the consolidating route, but problems related to the presence of trapped gases in flame- and plasma-sprayed coatings may limit the widespread adoption of this approach.

Surface alloying has been extensively studied at NRL, and at other institutions. This process consists of adding known amounts of other metals to the surface of a metal workpiece, laser melting and mixing these components, and allowing them to resolidify. The alloying elements have been added by several techniques including electro-deposition, vapor deposition, and by painting the surface with a slurry. Figure VII-1 shows a cross section through a low carbon steel which was coated with a thin layer of chromium and then laser-melted to produce a surface with corrosion resistance similar to that of a stainless steel. The dynamic polarization curves in Figure VII-2 demonstrate that in a 0.1 molar Na_2SO_4 solution the current density of chromium alloyed surfaces is substantially lower than the unalloyed steel. A chromium-containing stainless steel, such as type 430, would show a current density curve similar to the sample with 20%Cr. These results show that considerable savings in chromium usage could be effected by using surface alloyed steels (and other metals) in place of many of the bulk corrosion resisting materials presently employed by the military services.

The laser melt/particle injection process, which was developed at NRL, is illustrated schematically in Figure VII-3. This process consists of melting a shallow pool on the surface of a sample which is translated under a focused laser beam, and of blowing powder particles into the melt pool from a fine nozzle positioned about 1 cm away. The powder consists of either hard, wear-resisting particles which dissolve to only a limited extent in the melt, or metallic particles which are deliberately dissolved in the melt to accomplish surface alloying.

This approach is exemplified in the right photo which shows a cross section of a single melt pass on a Ti-6Al-4V sample which was injected with TiC particles. The bulging of the upper surface results from displacement of the base alloy by the injected particles.

Extended area coverage is produced by overlapping melt passes, as demonstrated in the lower figure which shows a cross section through 5050 Al which was injected with TiC in a series of 3 mm wide melt passes. The samples illustrated in Figures VII-4 and VII-5 are considered to be especially significant because it is particularly difficult to form wear resisting surfaces on these alloys. The only commercially available techniques for doing so at present involve depositing a hard coating over the metal, and adherence of the coating to the metal is always far from ideal.

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— 500 μm

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Fig. VII-1 — Transverse cross section of laser surface alloy with average
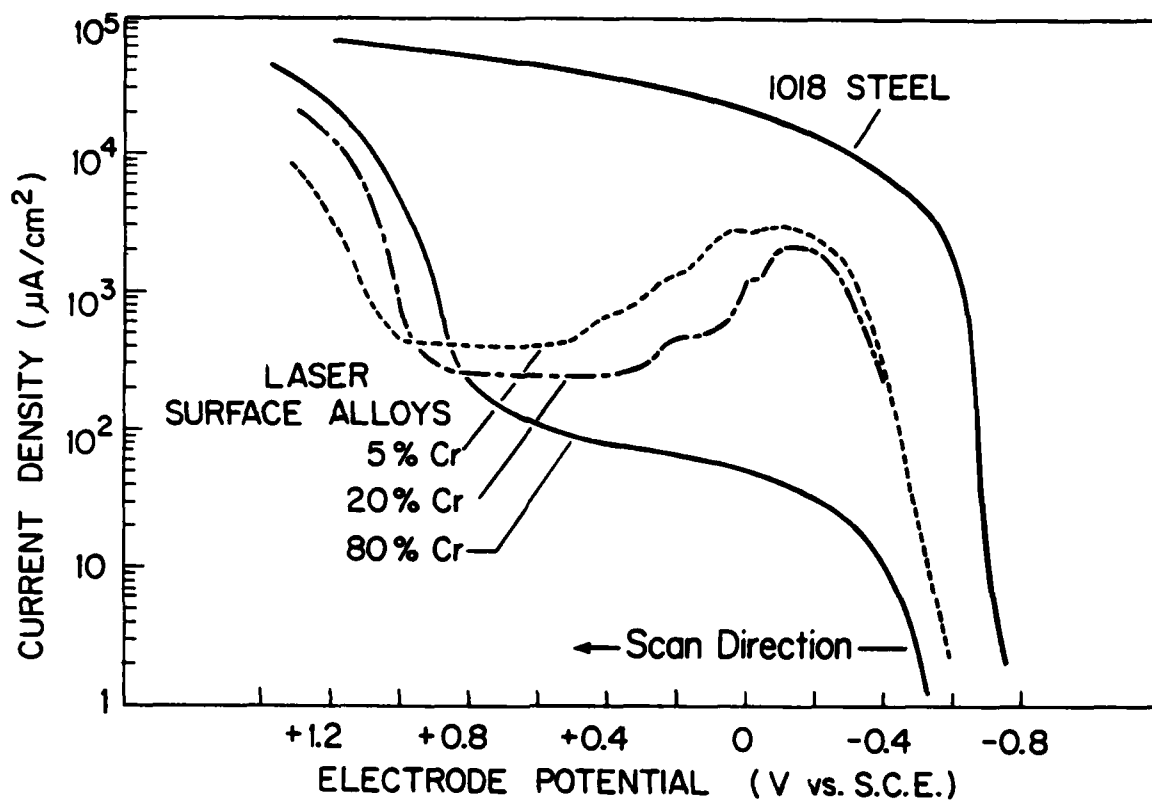Cr content of 16%, produced by successive, overlapping laser passes

Fig. VII-2 — Anodic polarization curves of laser surface alloyed steels
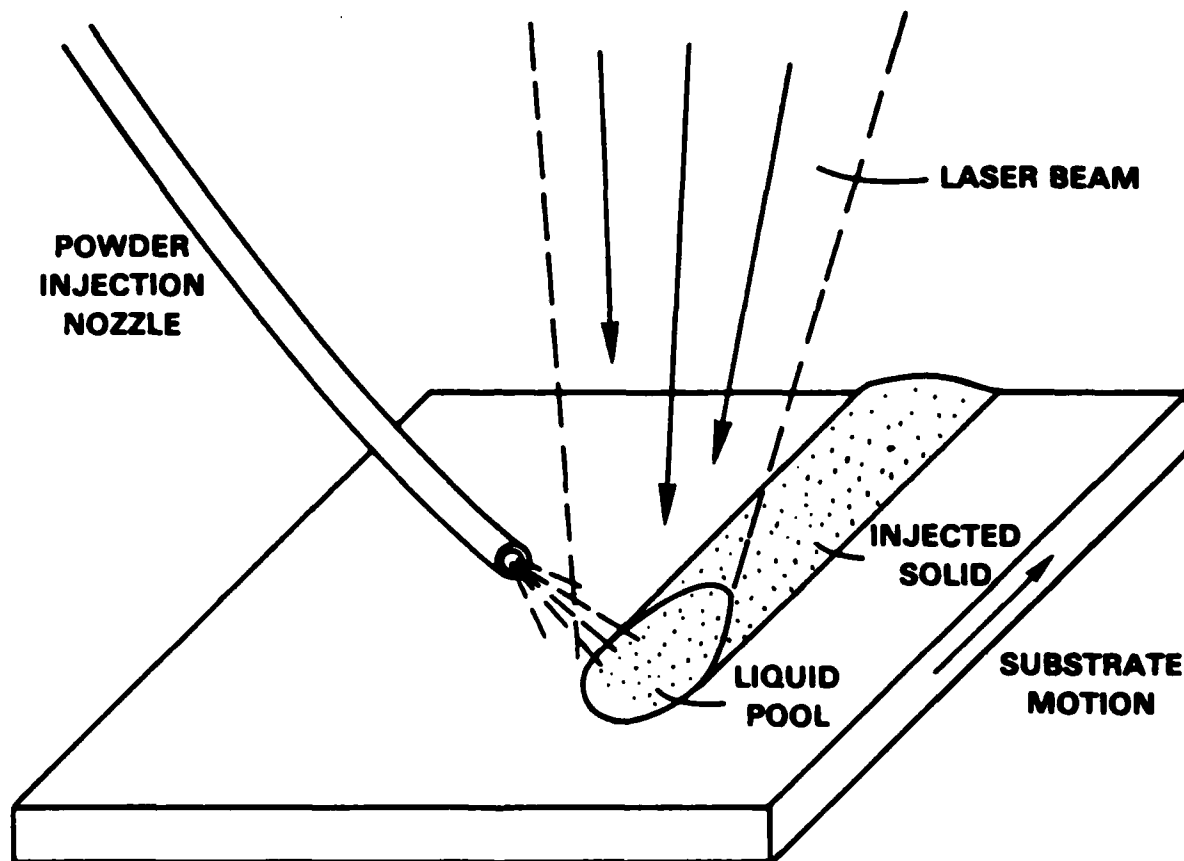in deaerated 0.1 molar Na_2SO_4 at 25°C

Fig. VII-3 — Schematic showing injection of particles into a melt zone established by a high-power laser. The particles are carried by a stream of helium.
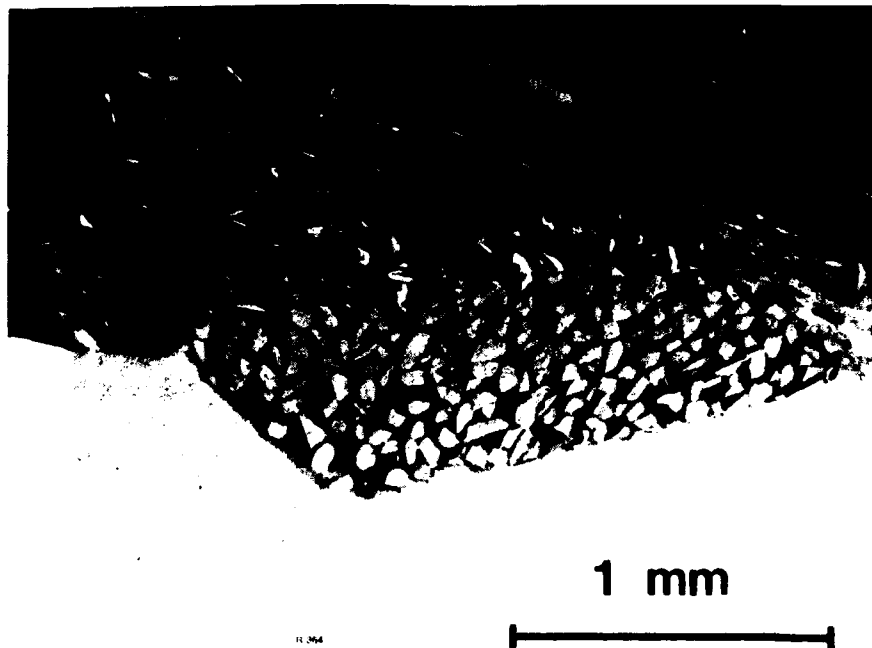
1 mm

Fig. VII-4 — Scanning electron micrograph of laser melt pass in a sample of Ti-6Al-4V injected with -170 +200 mesh TiC. This experiment used a laser power of 6 kw and a sample translation speed of 5 cm/s.
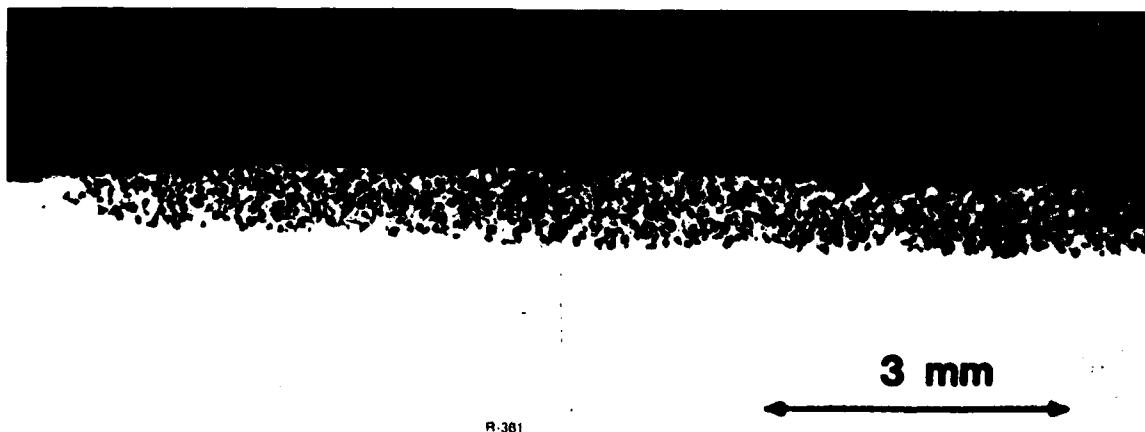

3 mm

Fig. VII-5 — Sectional view of 5052 Al injected with TiC. Sample was advanced 1 mm between melt passes.

This process has been used to produce wear-resisting surfaces on iron, nickel, titanium, aluminum, and copper based alloys injected with titanium carbide or tungsten carbide. Abrasive wear testing, done by the dry sand/rubber wheel technique, demonstrates that all of these alloys exhibit dramatically enhanced wear resistance. These results are shown in Figure VII-6, wherein the data to the right shows the depth of the wear scar produced on the alloy in the as received condition, and the data to the left shows the results after particle injection. Note that the aluminal alloy showed a two order-of-magnitude improvement in resistance to wear of this type.

As mentioned previously this process can be used to accomplish surface alloying by injecting powder of the alloying element directly into the base metal, thereby eliminating the precoating step in the processing. Alternatively, the processing conditions can be adjusted so that the beam melts just enough of the sample surface to weld down a coating which is built up from powder blown into the melt pool. This variation of the process is illustrated by Figure VII-7, which shows the cross section of low carbon steel sample which was clad with nichrome, a corrosion and oxidation resisting alloy. This processing produced a coating which was well bonded to the substrate and which was nearly free of pores - much more so than similar coatings produced by plasma spraying and other commercial processes.

In summary, the laser processing discussed here exhibits a high potential for lowering the cost of some materials used in military hardware, and for dramatically extending the service life of other materials, and it offers the promise of making possible the design of new light-weight equipment using Al and Ti alloys in application where wear problem have previously precluded their use.

Additional information may be obtained from:

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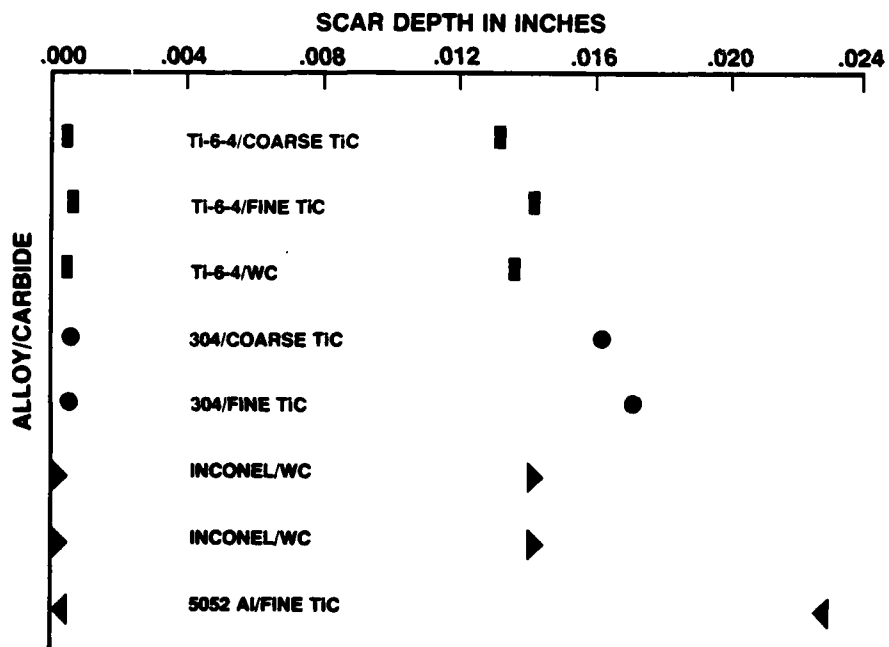Washington, D. C. 20375

SCAR DEPTH IN INCHES

Fig. VII-6 — Dry sand/rubber wheel wear test results on samples in as-received condition (at right) and after carbide particle injection (at left)
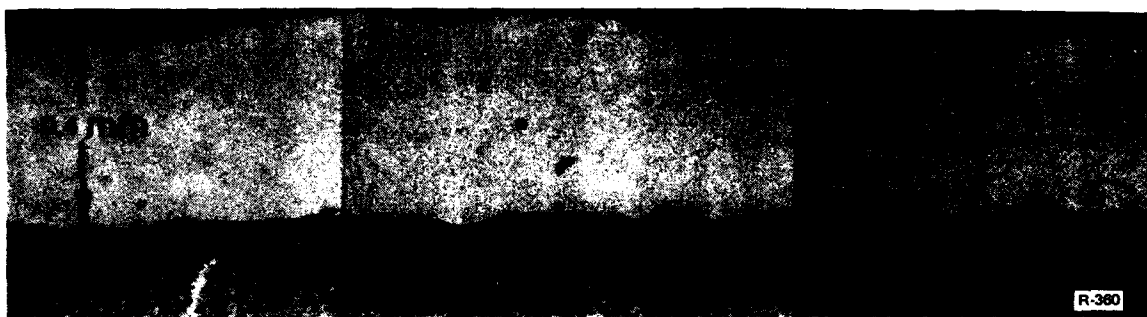
Fig. VII-7 — Surface of 1018 steel clad with nichrome by injection processing. The surface was clad at 5 kw smoothed by remelting at 4 kw.

VIII. Naval Aircraft Corrosion Control

There are a number of advances in materials and processes for naval aircraft corrosion control that are currently in use and others that are under development in the laboratory for future use. Those currently in use include:

(1) Water displacing corrosion preventive compounds for touch-up that dry to form a corrosion protection film for use in a marine environment.

(2) A return to anodizing for new weapons systems rather than chromate conversion coatings. Both sulfuric and chromic acid anodizing are being used. Anodized surfaces provide more corrosion protection, abrasion resistance and long-term durability than chromated surfaces.

(3) Aluminum alloys such as 7050 containing zirconium that replaces chromium, and lower concentrations of the tramp elements, iron and silicon, and which provide greater resistance to stress corrosion cracking with no sacrifice in strength.

Materials under development include:

(1) Water displacing paint: A pigmented coating, composed of a petroleum sulfonate, silicone - alkyd resin, organic solvents, pigments and other organic additives, which will displace water, dry and subsequently provide corrosion resistance. This finish protects the substrate from corrosion by: (a) the physical barrier of the coating, and (b) the corrosion inhibiting pigments, i.e., molybdates and chromates. These paints are for touching up painted surfaces at the Fleet level. Initial evaluation has been encouraging.

(2) Aluminum plating process: Aluminum has been found to be a very good alternative coating material in place of cadmium in many applications requiring good corrosion resistance and minimal effect on fatigue properties. Cadmium is being replaced because of its toxicity. Work is underway to develop a method to electroplate an aluminum coating from a molten salt bath. A coating of aluminum - manganese has been deposited on aluminum, titanium and steel substrates with conventional precreatments and with excellent adhesion. Work is in progress to optimize the plating parameters. Other methods were considered. Vacuum deposition has relatively poor covering power and adhesion is often only fair. Also, plating has better throwing power for coating of recesses and holes. Ion vapor deposition is proprietary and facilities for its application are complex.

(3) Phase Transfer Inhibitors: A method was developed by which ions could be solubilized in organic media using phase transfer catalysis. This method has been used to develop an entirely new vehicle for corrosion inhibitors - i.e., inorganic inhibitors incorporated in organic phases. These inhibitors have demonstrated improved corrosion protection. Laboratory tests also demonstrated that these inhibitors are effective in retarding crack growth rate of 4340 steel under fatigue loading in moist air.

(4) <u>Powder Metallurgy Aluminum Alloys</u>: Considerable work is in progress on aluminum alloys made by high density powder metallurgy processing rather than conventional ingot metallurgy practices of casting and working. The former materials have finer and more homogeneous microstructures, can be aged to considerably higher yield strength without losing their resistance to stress corrosion cracking, and have improved fatigue properties. These alloys could result in a significant weight saving in naval aircraft.

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