NAVAL RESEARCH REVIEWS

JUNE 1978

PROFILES IN SCIENCE

Professor Ernest Yeager

Since 1948 when Professor Yeager first joined the faculty of Western Reserve University, the Office of Naval Research has sponsored his research in physical acoustics and electrochemistry. Out of this research have come several new electroacoustic effects, the explanation for the 1 kilohertz acoustic relaxation in long range sound transmission in sea water, and the sodium amalgam battery which in the late 1950's was considered as a submarine power source. The ONR sponsored research of Professor Yeager and his students has contributed much to the present understanding of O_2 electrochemistry and particularly O_2 electrodes for fuel cells and batteries.

Dr. Yeager is the Director of Case Laboratories for Electrochemical Studies and Professor of Chemistry at Case Western Reserve University. He is past President of the International Society of Electrochemistry and past Vice President of the Acoustical Society of America. He has served as a member of the Committee on Undersea Warfare of the National Research Council, The Underwater Sound Advisory Group of the U.S. Navy, and the ARPA Technical Power Panel. In 1972 he received the Navy Certificate of Commendation.

Naval Structural Materials: Requirements, Issues, and Opportunities

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Introduction

The advancement of structural materials technology over the remainder of this century poses one of the more important and certainly one of the most challenging areas of Naval research and development. (This forecast is based on well defined trends of Navy and Marine Corps systems development.) Foremost among these trends is the pervasive and often critical role structural materials play in defining the military effectiveness of Naval vehicles and weapon systems. Most often, the development of new and improved operational capabilities is dependent in varying degrees on the development of new and improved materials performance. In addition, there are urgent requirements for structural materials and production techniques which will improve availability, damage tolerance and survivability, while reducing cost of most major systems.

Another indicator of the potential impact of structural material technology on future systems comes from the pairing of key technical issues and R&D opportunities. Here, the picture which emerges is one of the accelerated applications of the interdisciplinary approach of modern material science to the development of new and improved structural materials technology and the accelerated transfer of this technology to the design, fabrication, and maintenance schedule of future systems. In many ways, our ability to supply improved and innovative structural materials in a timely and affordable way will be an important factor in determining the types, numbers and mix of future vehicles and platforms.

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In the two following sections of this article, the above theses are developed from complementary perspectives. First, the relationships between structural material requirements and operational capabilities are examined for the following Naval systems: (1) future high performance ships, (2) next generation V/STOL aircraft, and (3) current conventional ships. These systems are selected for review because of the differences in their time frames for operational deployment. In the second major section, the viewpoint of the materials technologist is assumed. Here, the technical issues and R&D opportunities are explored for the following generic classes of structural materials: (1) high strength marine alloys, (2) thermostructural alloys, and (3) advanced composite materials. These discussions provide examples of structural materials development at various stages of technological maturity and therefore at various proximities from system impact. From these admittedly incomplete surveys, it is hoped that the diversity and complexity of the challenges facing the Navy's structural materials community over the next several decades will become apparent.

Structural Material Requirements of Selected Naval Systems

High Performance Ships

High performance hydrofoils, surface effect ships (SES), air cushion vehicle (ACV) and other advanced vehicles utilize structural and machinery materials to their performance limits. The primary operational utility of these vehicles in comparison with conventional ships is their high speeds and in some cases enhanced sea-keeping behavior. Depending on the lift and installed horsepower of various designs, these vehicles have demonstrated and projected speeds in the range of 50 to 100 knots. However, because of the high horsepower and high specific fuel consumption, the payloads of these vehicles are penalized relative to conventional designs. The so-called useful load (fuel and payload) of advanced ships, approximately 50% of the full gross weight, is strongly dependent on the structural weight fraction and to a lesser extent on machinery and lift system weights. Accordingly, the operational capabilities of advanced ships are dependent on the availability of high performance structural materials.

To date, advanced ships built by the U.S. Navy have been test and evaluation platforms (SES-100 and PCH-1 hydrofoil) and special purpose craft (PHM hydrofoil) of 50 to 200 tons. The hull structures of these craft are predominantly welded construction of marine

aluminum (5000 series). The struts and foils of hydrofoil craft have utilized a variety of high strength alloys, including HY-steels, PH stainless steels, and titanium. Although materials problems have appeared in these applications, the general materials performance is judged as adequate.

By contrast to existing vehicles, far-term (Circa 2000) advanced ship designs are perceived as large (1,000 to 10,000 ton), high speed (50–100 knot) open ocean combatants. As indicated by the structural weight fraction vs. gross tonnage trends of Figure 1, the advanced design concepts appear as near-level extrapolation of the smaller existing vehicles; and in fact, the advanced designs are based on current structural materials and fabrication technology. Because structural efficiency is expected to increase with size, it could be concluded that the advanced vehicles are conservatively designed with regard to structural weight and structural integrity. However, this conclusion is premature for any one of several factors.

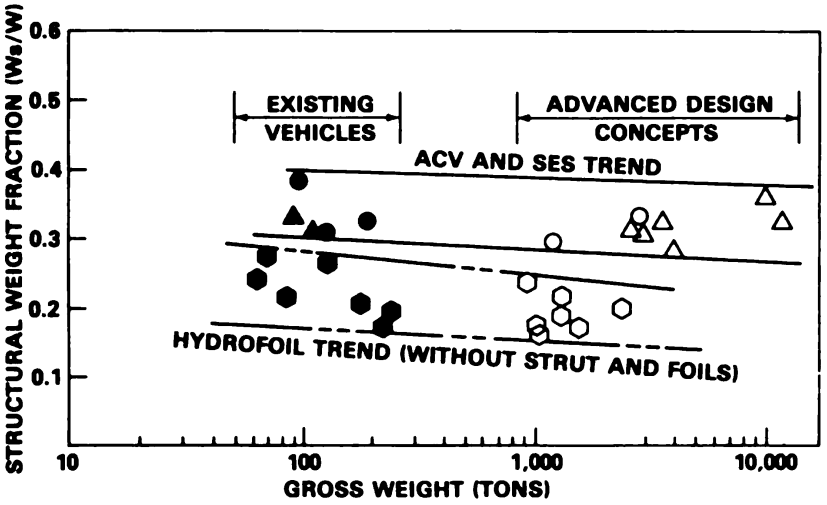

Figure 1 – Comparison of structural weight fraction versus gross weight for existing (closed symbols) and advanced design concepts (open symbols); air cushion vehicles, ACV, ○; surface effect ships, SES, △; and hydrofoil, ⬡ .

As high value combat platforms, the advanced concepts must contain a greater degree of damage tolerance than existing vehicles. These requirements include ballistic armor (directly substituted in the SWES-100 structural weight) and fire barrier protection of the aluminum structure. Hence, in order to incorporate the added damage tolerance requirements without sacrifice of operational performance in future large high performance ships, some combination of the following improvements must be effected: (1) reduction in

weight of structural and machinery components; and/or (2) use of materials in a multifunctional design—e.g., integrated structure/armor/fire-barrier material.

Also implicit in the design approach of large high performance ships is the assumption that operational loads can be defined to an accuracy approaching that used in modern aerospace designs. Indeed, the advanced ship design concepts are not unlike those used in a modern air transport (e.g. C-5A) predominantly of aluminum construction with a gross take off weight of approximately 300 tons, and a structural weight fraction between 0.35 and 0.40. However, high performance ships do not have the benefit of the highly redundant, crack arresting features of aircraft riveted construction. In the all welded aluminum construction of high performance ships, precise load information is required to ascertain the adequacy of current materials and design practices for potentially severe, but as yet unknown, advanced design materials problems such as high-cycle, low amplitude fatigue. At this time, however, load definition and material performance for large, high performance vehicles cannot be determined with a high degree of confidence from the design and operational experiences of much smaller vehicles. Hence, design optimization and structural life management concepts will require considerable R&D efforts, including adequate lead time and experience with full scale prototypes.

V/STOL Aircraft

Very similar to advanced ship concepts, the improved operational capabilities of future V/STOL aircraft present an open-ended challenge to materials technology. As is well known, the vertical/short takeoff and landing (V/STOL) capability provides the Navy with the option of deploying combat aircraft from a greater number of smaller, less costly and more responsive carriers and air-capable ships. Some estimates predict an all V/STOL inventory for the Navy and Marine Corps near the turn of the century. Similar to the high performance ships, the range and payload of V/STOL aircraft are curtailed relative to conventional carrier aircraft. The most direct approach to improving the operational effectiveness of future V/STOL aircraft is the introduction of improved materials and design concepts in either or both the airframe and the engine.

In the case of the airframe, a revolutionary use of advanced composite materials is projected for future V/STOL aircraft. Basically, an advanced composite consists of high strength/stiffness fibers bonded in a polymeric or metallic binder (matrix). The relationship between

structural weight reduction and percent of composite materials are shown in Figure 2. Notwithstanding the efforts of the other services and NASA in composite materials development, the Navy's F-18 lightweight fighter and the Marine Corps' AV-8B advanced harrier (V/STOL) represent the state-of-art usage of advanced composites in airframe structures. As indicated in Figure 2 the projected use of advanced composites in next generation of V/STOL aircraft truly represents a radical departure in aircraft structural design. The projected weight saving will make the useful load/total weight ratio of V/STOL aircraft approximately equivalent to that of conventional aircraft.

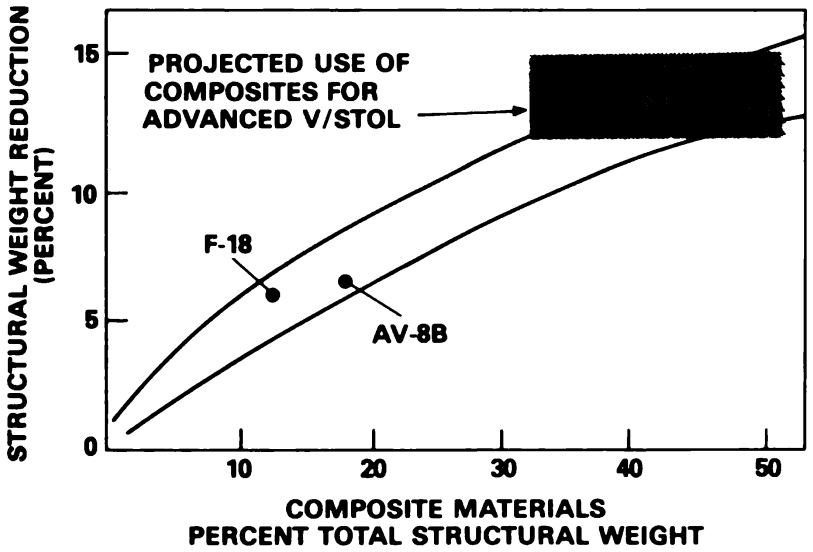

Figure 2 – Relationship between structural weight reduction and composite material usage in advance airframe structures. Projected use of composite materials for advanced V/STOL requirements indicated.

The development of thermostructural materials for high temperature engine applications is also a viable approach to improved operational capabilities of V/STOL aircraft. The basic goal here is to increase range and/or specific thrust (HP/lb) by a lower specific heat rate turbine operation. This can be accomplished by (1) an increase in turbine inlet temperature or (2) a reduction of air volume used for cooling. As shown in Figure 3 significant gains in gas turbine efficiency have been made over the past three decades by combinations of the two approaches. The payoff in air cooling, however, appears to be one of diminishing return. Realization of higher inlet turbine temperature, therefore, equates with increasing the allowable metal temperature for turbine components above the current 1000°C limit of superalloys (Figure 3).

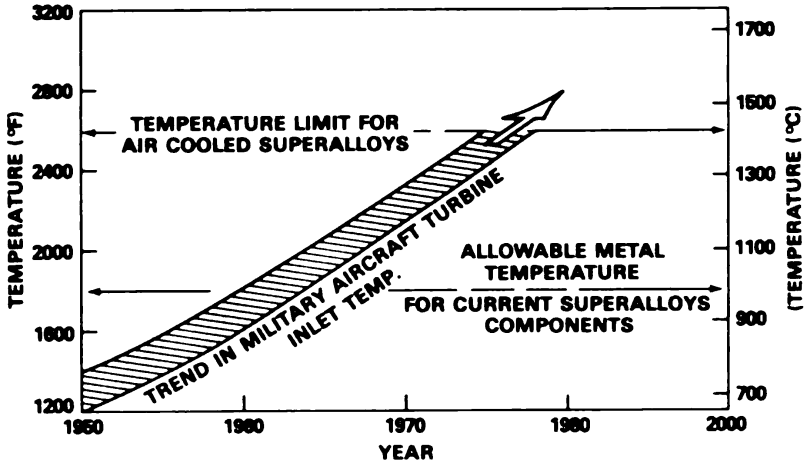

Figure 3 – Trend in military aircraft turbine inlet temperature; and allowable metal temperature for current superalloys.

Because of the complexity of high temperature service behavior of thermostructural materials and because of the critical consequences of engine failure, the introduction of new materials will be more evolutionary than revolutionary in nature. Nonetheless, the payoffs are significant. For example, a simple extrapolation of the trend shown in Figure 3 indicates a 300°C increase in turbine inlet temperature before the turn of the century. Depending on type of engine, this increase equates to a 20 to 50% increase in specific thrust.[1,2,3]

Conventional Ships

Notwithstanding the development of high performance ships, V/STOL aircraft and other advanced concepts, it is a reasonable assumption that the majority of ships in the fleet inventory at the turn of the century will be derivatives of current designs. Although the development of these systems will also be evolutionary in nature, the potential impact of structural material technology is no less diminished. This supposition is supported by the large number of systems which benefit from improvement in materials technology. Moreover, current trends indicate a shift of priorities and R&D emphasis from performance requirements to other factors affecting military-worth, such as damage tolerance and survivability, availability, and that nemesis of defense systems-cost.

The requirement for improved damage tolerance and survivability was made apparent in the 1975 collision of the aircraft carrier JFK and the cruiser BELKNAP. The melted remains of the cruiser's aluminum superstructure are shown in Figure 4. Only the steel frame

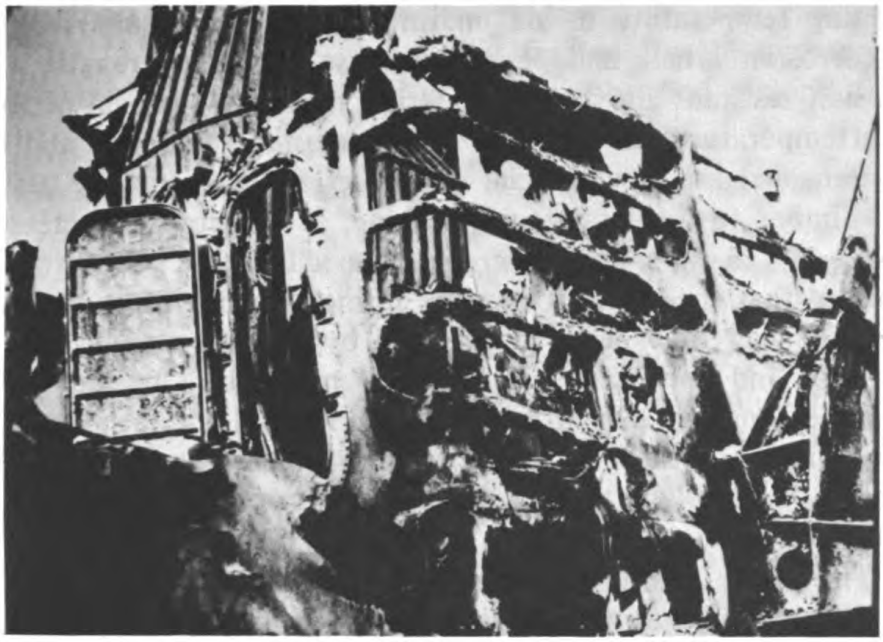

Figure 4 – The fire damage of the aluminum superstructure of the cruiser BELKNAP after collision with the aircraft carrier JFK in 1975.

remains erect. The lightweight aluminum superstructure of conventional ships is a post World War II innovation and, therefore, has not been combat tested. Moreover, fire hazard susceptibility as well as ballistic damage tolerance were also cited as issues in the the combat worthiness of the predominantly aluminum construction of advanced surface ships. Hence, the continual development and innovative use of affordable fire resistant coatings, insulation materials, lightweight armor and improved structural materials are required to sustain the improved performance obtained by aluminum alloys in ship construction.

Another example of the potential impact of materials technology on conventional ship development is provided by the marine gas turbine – the adopted prime mover of U.S. Navy nonnuclear surface ships. The development approach of the Navy's marine gas turbine has been to modify existing aircraft turbojet engines. The approach was dictated by the prohibitive cost of developing an altogether new engine.[2] The life limiting factor of marine turbines is the sulfidation/oxidation (hot corrosion) of components in the high temperature turbine sections. Hence, the major modifications in the so-called "marinizing" of aircraft gas turbine are the substitution of more sulfidation/oxidation resistant materials and the reduction of operating temperatures from those of the aircraft engine. The reduced

operating temperature of the marine gas turbine results in lower hot corrosion attack and permits the use of lower strength, more corrosion resistant alloys. The materials tradeoffs between performance (temperature), availability (hot corrosion resistant), and cost (maintenance) are most crucial in the design of the marine gas turbine. Similar to the aircraft gas turbine, a temperature increase of 50°C results in 4-8 percent increase in specific trust. However, it is estimated that the resulting increase in metal temperature would reduce the mean time between overhaul by tens of percent.[2] The magnitude and importance of the problem can best be appreciated when one considers current performance levels. The mean time between failures of the marine gas turbine engine is a major limiting factor in the availability of surface ships propelled by this power plant.

The above commentary on high performance ships, V/STOL aircraft, and conventional ships is intended to illustrate the structural materials requirements of far-term, next generation, and operational systems, respectively. These discussions could have included other important and equally materials dependent systems, such as submarines, missiles, amphibious and armor vehicles. Rather than extend these discussions, however, attention is now directed toward technical issues and R&D opportunities associated with Naval structural materials. More specifically, these factors are addressed in the following section for (1) high strength marine alloys, (2) thermostructural materials, and (3) advanced composite materials. As previously noted, these materials are representative of structural material developments with near- to far-term impact.

Technical Issues and R&D Opportunities Of Naval Structural Materials

High Strength Marine Alloys

The structural efficiency of alloys and weldment systems is directly proportional to allowable design stresses at which these materials can be incorporated into a structure. The design stresses for commercial high strength alloys, however, are typically a fraction ($\sim$1/4 to 1/2) of the yield strengths which in turn are only a fraction of the strengths which are metallurgically obtainable. The seemingly conservative (low) working stresses of high strength alloys are dictated by other engineering requirements, principally

Fracture Toughness	– the resistance of a material to unstable fracture in the presence of localized embrittled regions, flaws, or cracks
Crack Growth Tolerance	– the resistance of a material to subcritical crack growth under service conditions; e.g., sustained or cyclic loading in a marine environment
Corrosion Inhibition	– the resistance and/or protection of a material to degradation effects of electrochemical attack

The design trade-off between strength and fracture toughness of high strength alloys is one of the classical problems of modern engineering materials. Simply stated, the fracture toughness of these alloys decreases as the strength is increased by conventional processing – heat treatment, alloying, and mechanical working. Hence, at a sufficiently high working stress/strength ratio, structural alloys will be unacceptably susceptible to catastrophic brittle fracture. Over the past several decades, quantitative measures of fracture toughness and rational principles of fracture control design have been developed, starting with the pioneering work of Irwin[5] and of Pellini[6] and their co-workers at NRL in the late 1950's and early 1960's. These developments not only have had far ranging ramifications to the structural integrity of military and civilian structures but has also opened up new vistas of R&D opportunities which have only begun to be realized.

In particular, the ability to quantitatively predict the behavior of an alloy offers the opportunity to optimize the following property/requirement trade-offs listed in Table I. Such a capability is extremely valuable in the demanding and complex materials requirements of marine structures.

A quantitative example of the relationship between strength, crack tolerance and corrosion resistance for a precipitation hardened stainless steel (17-4 PH) is given in Figure 5.[7] This alloy has been utilized for specialized purposes in aircraft and rocket components and in certain marine applications like struts and foils for hydrofoils because of the alloy's relatively good corrosion resistance at high strength levels. The data of Figure 5 show the effects of electrochemical potential coupling on the stress corrosion cracking resistance of this alloy, heat treated to various strength levels. Stress corrosion cracking (SCC) resistance of an alloy is related to the

TABLE I	
Property	Requirement
Strength	Performance
Fracture Toughness	Reliability, damage tolerance
Crack Tolerance	Reliability, damage tolerance
Corrosion Resistance	Cost, availability

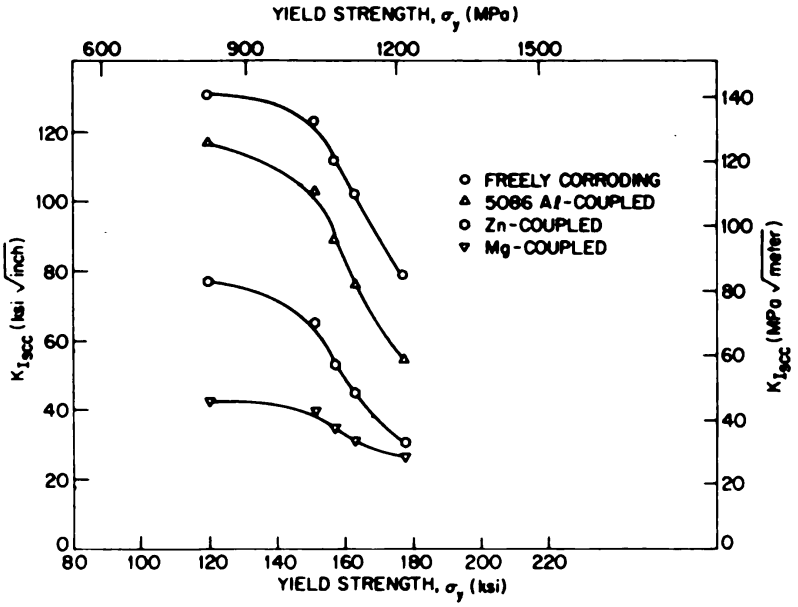

Figure 5 – Stress corrosion cracking data for high strength stainless steel (17-4PH) of different yield strengths under four electrochemical conditions (Ref. 7).

initiation and growth of a crack at stress concentration sites in the presence of a corrosive environment, and is measured by the fracture mechanics parameter K_{Iscc}. This parameter defines a threshold crack-tip stress state below which SCC will not occur in the test environment. Usually, the critical stress intensity value of K_{Iscc} for SCC is determined experimentally from sustained-load tests conducted on relatively small precracked specimens immersed in salt-water.

The upper curve of Figure 5 illustrates the decrease in SCC resistance for increasing strength levels under freely corroding conditions. The lower curves show the effects of changing the electro-

chemical potential by coupling to aluminum, zinc and magnesium. The coupled materials are similar to anodes used in corrosion protection of marine structures.

If the positive directions of the horizontal and vertical axes of Figure 5 are equated to increased performance (strength) and increased structural reliability (K_{Iscc}) respectively, and if the negative coupling parameter is equated to decreasing maintenance costs (corrosion protection), these data are indicative of the materials selection trade-offs facing the designer of marine structures. Namely, what windows in Figure 5 represent the optimum utilization of an alloy in specific applications? When coupled with improved understanding of the basic mechanisms of SCC, this type of materials characterization will also provide a basis for the development of improved alloys, as well as improved fabrication and inspection techniques.

An even more ubiquitous limitation of high strength marine alloys than SCC behavior is their fatigue and corrosion fatigue resistance. Unlike the SCC behavior, however, the fatigue crack-growth resistance of structural alloys is relatively insensitive to strength level. In many applications, however, the fatigue properties of alloys determine the allowable design stress and, thereby, preclude the use of alloys above a certain strength level.

The characteristic material property describing fatigue crack-growth resistance is the per-cycle crack growth da/dN as a function of the fracture mechanics parameter ΔK, the magnitude of the stress intensity excursions during the cyclic loading. In addition to its utility as a direct measure of fatigue crack growth resistance, the da/dN vs. ΔK relationship can be used to predict service behavior and, thereby, prevent failure by containment of crack growth within quantitative safe limits. The rationale and methodology for using fracture mechanics fatigue design are discussed in Ref. 8.

Although fracture mechanics methods of predicting fatigue behavior are now used in the design process, understanding the mechanical, metallurgical and electrochemical factors affecting fatigue crack growth resistance and the transitions of this understanding to improve or to optimize alloys has only begun to be explored and exploited. For example, the varied effects of seawater environment and electrochemical potential coupling on the fatigue behavior of three marine alloys are shown in Figure 6.[9] In the case of the 17-4 PH stainless steel, seawater environment and negative potential significantly decrease the fatigue crack growth resistance of this material. The marine aluminum alloy (5456-H116) also exhibits a deleterious effect of seawater on fatigue crack growth behavior; but both negative and positive potential from the freely

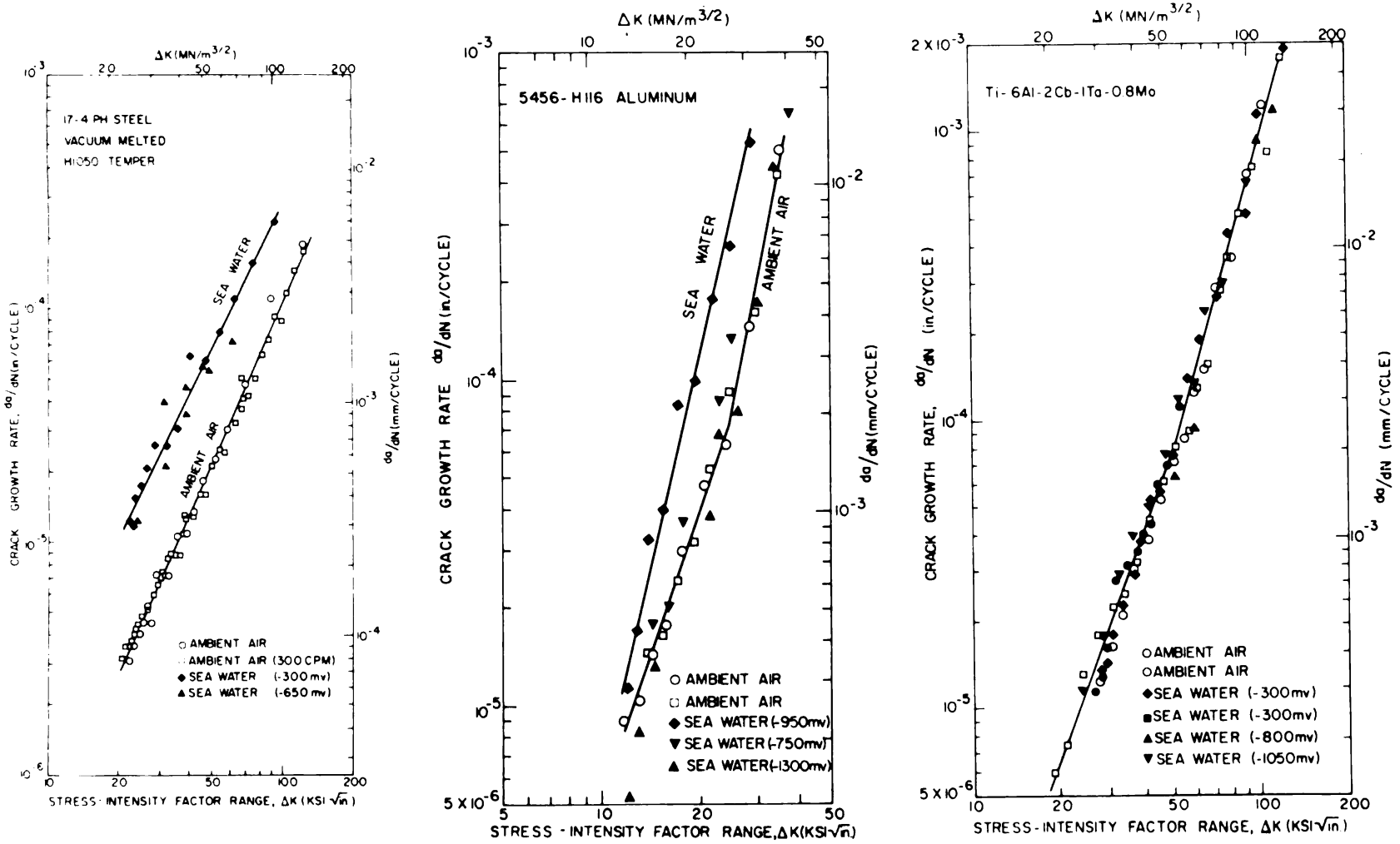

Figure 6 – Comparison of fatigue crack growth data for three marine alloys under ambient air, seawater and potentiostated conditions (Ref. 9).

corroding potential of approximately -1.0V have the beneficial effect of decreasing the fatigue crack growth rate. In fact, a fatigue crack growing in the freely corroding condition has been observed to be abruptly terminated when the specimen was polarized cathodically to -1.4V.[10] The basic electrochemical and micromechanical processes controlling these phenomena, as well as the engineering ramifications of these results, are not now well understood. In contrast to the ferrous and aluminum alloys, the fatigue behavior of the titanium alloy is not affected by either seawater or negative potential, attesting to the superior performance of this class of alloys in marine applications.

Notwithstanding the superior performance of titanium alloys, recent research efforts[11] have significantly improved the fatigue crack growth resistance, fracture toughness and SCC resistance of several titanium alloys through microstructural modifications. As shown in Figure 7 for example, the da/dN vs. ΔK curves are distinctly altered by their heat treatment. The conventional mill-anneal alloy, typical of most alloys in service, exhibits much higher fatigue crack growth rates than the less conventional beta-anneal alloy. The improvement in fatigue crack growth resistance, nearly an order of magnitude between the two alloys at the lower range of ΔK, was accompanied by a 12% decrease in strength. Using the predictive methods of fracture mechanics, however, this tradeoff can be shown to significantly increase the life of structural components in fatigue critical designs. Moreover, the beta-annealed alloy has also been shown to be far superior in fracture toughness and SCC resistance.

Not only can the engineering significance of the da/dN vs. ΔK data of Figure 7 be quantitatively evaluated, but the improvement in fatigue behavior can be rationalized in terms of the accompanying microstructural modifications and crack tip stress state as defined by the ΔK parameters. The difference in microstructure produced by the two heat treatments is shown in the micrograph inserts in Figure 7. The mill-anneal alloy has elongated grain structure induced during the rolling operation. The beta anneal alloy has the distinctive Widmanstätten or basket-weave microstructure. The improvement in fatigue resistance is most pronounced at the lower range of ΔK. At this ΔK level, metallographic and fractographic examinations of spent fatigue specimens reveal that the fatigue crack branches in multipaths along preferred crystallographic orientation within the Widmanstätten microstructure. This crack branching reduces the effective crack tip stress intensity and, thereby, reduces the crack growth rate. In contrast, the crack path in the mill-anneal alloy proceeds in a straight, transgranular manner. A comparison of the two

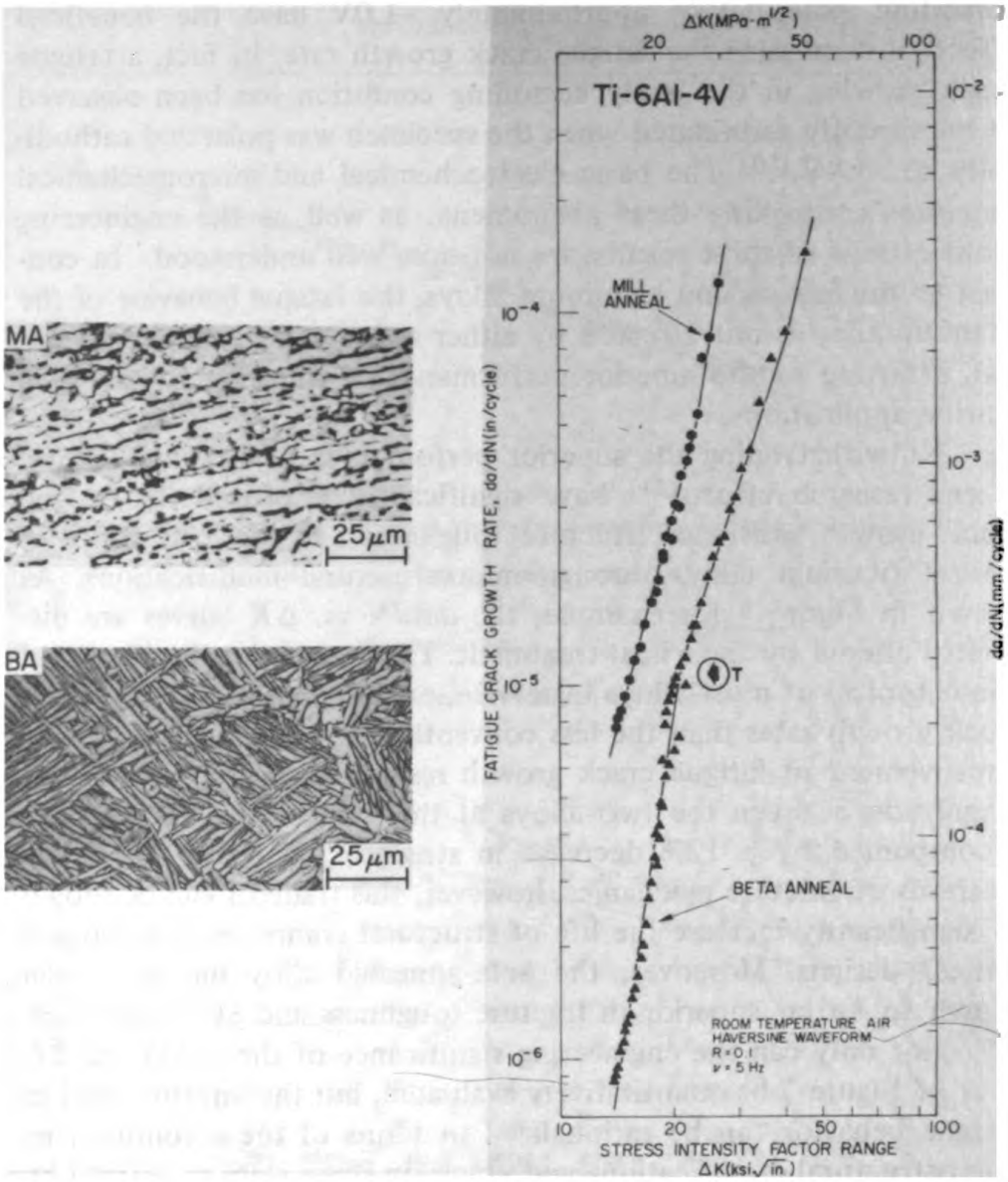

Figure 7 – Fatigue crack-growth rates and microstructure for mill anneal (MA) and beta anneal (BA) titanium alloys (Ti-6A1-4V) (Ref. 10).

modes of crack growtn is shown in the macrographs of Figure 8. At high values of ΔK the crack branching within the Widmanstätten packets and the corresponding beneficial effects on fatigue crack growth resistance (Figure 7) are diminished by localized plastic deformation at the crack tip.

In summary of this section, it can be confidently forecasted that the further development of rational principles for the metallurgical optimization of structural alloys and weldments offers R&D opportunities to improve the performance and cost of future Naval platforms and vehicles. By combining quantitative predictive meth-

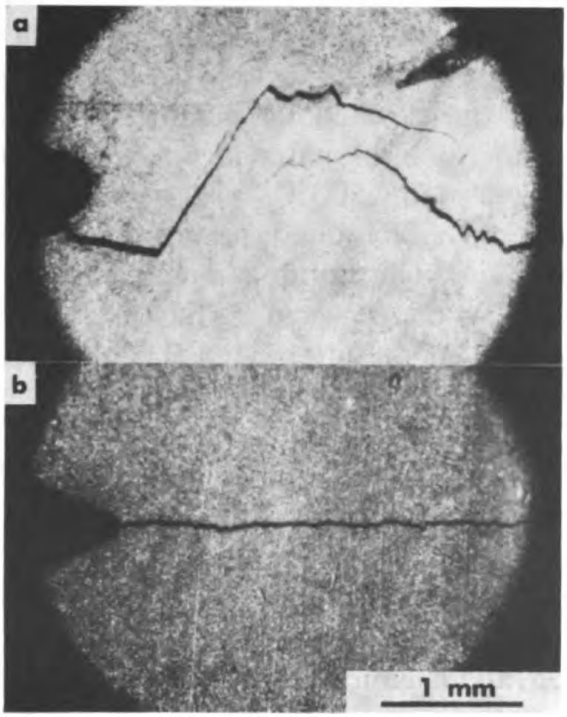

Figure 8 – (a) Crack bifurication in the fatigue crack path of a beta annealed Ti-6A1-4V alloy; (b) normal nonbifuricated crack in the fatigue crack path of a mill-annealed Ti-6A1-6V-2S alloy (Ref. 11).

ods, such as fracture mechanics analysis, with modern techniques of metallurgical control and microstructure characterization, structural alloy and weldment systems can be designed to meet specific operational requirements. This approach should yield the greatest benefit in the development of improved weldment systems, providing a larger selection of design options than is currently available. In addition, this capability will provide for the expeditious evaluation and accelerated development of new processing and fabrication procedures, such as laser welding, laser surface heat treatment and alloying, plasma spraying, and surface modification by ion-implantation. In all cases, the strategy will be to improve the critical crack tolerance properties at progressively earlier stages of the failure process – proceeding from improvements in fracture toughness to improvements in subcritical crack growth resistance and hence to improvements in crack initiation resistance.

Thermostructural Materials

The development of improved thermostructural materials for gas turbine and other high temperature applications requires an

exacting balance of properties, similar to high strength marine alloys, except for the added complication of the highly reactive and strength degrading effects of the elevated temperature environment. In this commentary, thermostructural materials are defined as load bearing materials used in excess of 500°C, i.e., beyond the temperature limits of titanium alloys. Required properties for these materials include low creep strain, high rupture strength, thermal and mechanical fatigue resistance, oxidation and sulfidation resistance, and impact resistance. Moreover, the interactions between these properties, as well as their engineering design tradeoffs, are even less understood than in marine alloys.

As previously described, the most pressing Naval requirement for improved thermostructural materials is associated with the hot gas path sections of both marine and aircraft gas turbine engines, especially the rotor blades. These life limiting components are simultaneously subjected to high centrifugal loads, thermal and mechanical fatigue, erosion, and chemical attack of hot gases. The pursuit for higher inlet temperatures of gas turbine blades has taken three primary approaches – (1) blade cooling, (2) improved materials and (3) coatings. The advent of air cooled blading represents a major advance in gas turbine efficiency, allowing an increase of 300°C in the turbine inlet temperature. However, this approach appears to have plateaued; and further improvements now point to advancements in materials and coatings or combinations of the two.

A probable sequence of advanced thermostructural materials for gas turbine blades include:

(i) directionally solidified superalloys
(ii) single crystal superalloys
(iii) directionally solidified eutectics
(iv) oxide dispersion strengthened alloys
(v) reinforced superalloy composites
(vi) refractory alloys
(vii) ceramics

The rupture life data shown in Figure 9 provide a first order estimate of the potential of these candidate materials to raise the turbine inlet temperatures above the current limits of conventional superalloys.

The potential improvement in the high temperature performance of the first three alloys of the above list can be related to specific microstructural features. In the case of the directionally solidified alloys, controlled casting procedures are used to develop a preferred grain structure orientation which minimizes the weak-link transverse

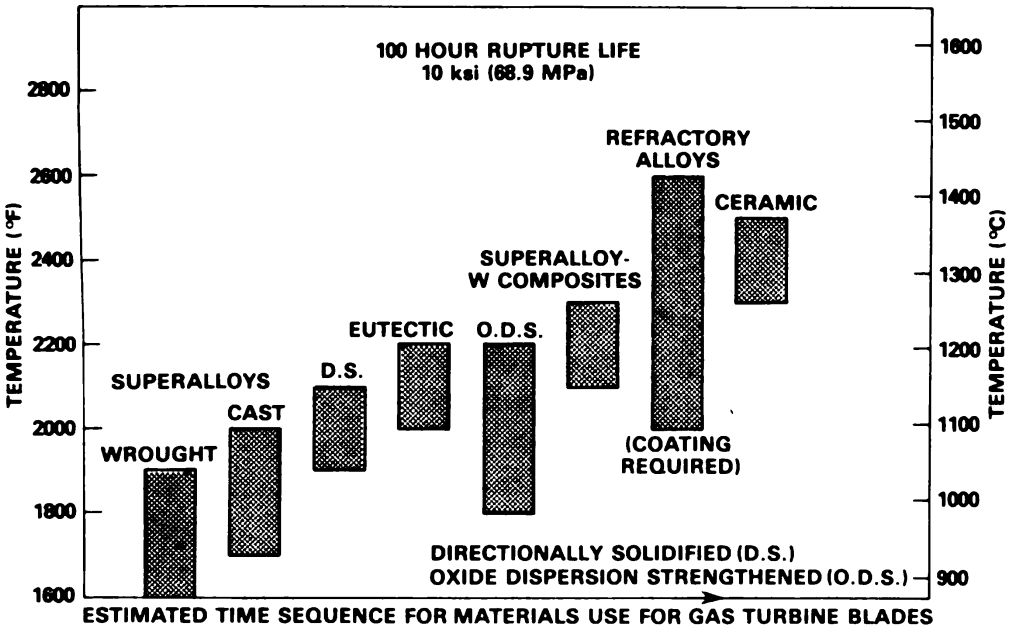

Figure 9 – 100 hour rupture life data for advanced thermostructural materials.

grain boundaries. Significant gains in low cycle fatigue and creep-rupture strength have been reported for these alloys.[4,12] A natural extension of this approach leads to a single-crystal blade concept which is also under active investigation. Similarly, the directionally solidified eutectics, or so-called in-situ composites, derive their strength from unidirectional fibrous or lamellar phases in nickel or cobalt base alloys. For example, the lamellar microstructure of the $\gamma/\gamma' + \delta$ directionally solidified eutectic is shown in Figure 10.[13] This alloy consists of δ-Ni_3Nb platelets in the γ-NiCr matrix and γ'-Ni_3Al solid state precipitates in the γ-NiCr matrix. Significant improvements in creep rupture strength over conventional superalloys have been reported for this class of alloys.[13,14]

Dispersion strengthened and reinforced superalloy composites, number four and five on the above list, also offer viable alternatives to advanced alloy development. In the first case, powder metallurgy processing is used to produce a uniform, submicron oxide dispersion (e.g., of ThO_2 or Y_2O_3) in nickel, iron or cobalt based alloys. These alloys have inherently higher strength near melting temperatures and also have been shown to have higher creep rupture strength than conventional precipitation-hardened alloys at temperatures in excess of 1100°C.[4,15] In the case of the reinforced superalloy composites, continuous fibers of high strength tungsten, typically 20 mils in diameter, are used to reinforce nickel based alloys through casting or solid state bonding methods. Although the high density of the tungsten fiber, constituting as much as 20 to 70 percent volume fraction

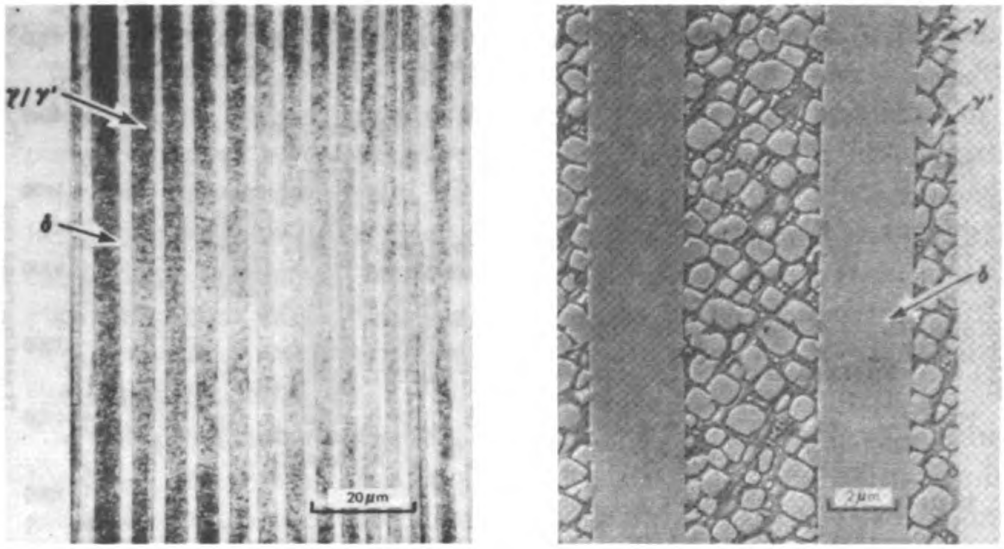

Figure 10 – Microstructure of the $\gamma/\gamma' + \delta$ directional solidified eutectic.

of composite, penalizes this approach, significant improvement in 100 hours rupture strength is obtained as is in Figure 9.[4,16]

In this seemingly open ended quest for high temperature materials, one is ultimately led to the consideration of the last two candidates on the above list, the refractory alloys and ceramics. The high intrinsic melting temperatures of refractory alloys are countered by their high density. The most promising prospects appear to be alloys of niobium and molybdenum. Although commercial alloys of these refractory elements are available, their poor oxidation resistance prohibits their use in gas turbine applications. As with other classes of advanced turbine alloys, refractory alloys will most likely require some type of compatible protective coating. The engineering utility of corrosion resistant coatings (i.e., durability, cost, etc.) is an uncertain factor in the development of advanced thermostructural alloys.

In contrast to refractory alloys, ceramics have low density and improved hot corrosion resistance. Some ceramics are under investigation as candidates for corrosion protection coatings of advanced alloy systems. In addition, the high sublimation temperatures and high temperature strengths of ceramics offer the largest potential gains in turbine inlet temperature of any uncoated advanced material. Although the payoff for ceramics appears most promising, the associated technical problems are quite formidable. Foremost, even the most promising thermostructural ceramics, such as silicon carbide and silicon nitride, are highly flaw sensitive, ductility limited materials. Accordingly, an improved or altogether new design approach must be developed to effectively cope with the ductility limitations

of ceramics. In addition, the engineering utility of ceramics for gas turbine applications also depends on a high degree of quality control in all phases of material life cycle – constituent preparation, processing, machining, fabrication and in service inspection. Excellent reviews of the state-of-art of ceramic material for gas turbine applications are given in Refs. 17 and 18.

The above cursory discussion indicates the variety of thermostructural materials under active development for gas turbine and other high temperature applications. Although each candidate class of materials has shown specific advantages over current state-of-art superalloys, much remains to be done before these materials realize their potential. For example, it is estimated that a major impact of ceramic as a gas turbine material is at least 20 years away.[17] The necessity and utility of protective coatings for advanced thermostructural alloys are an unknown commodity at this time. In addition, compatible high temperature lubricants and bearing material must be developed in parallel with improved thermostructural materials. Another complicating factor in the development of thermostructural materials is that the utility of quantitative analyses, such as fracture mechanics, in the characterization of thermostructural materials has just begun to be investigated (see for example Ref. 19). Traditionally, design and service life prediction of materials in high temperature applications are based on conservative, more empirical methods than those used in aerospace or even marine structures. In fact, the future development of improved thermostructural materials for gas turbines will most likely progress in an iterative manner with the development of more rational design analyses, service life prediction methods and inspection techniques. In general, the introduction of advanced materials in high performance systems requires an improvement in all the latter aspects of material technology in order to avoid the catastrophic consequences of engine failures.

Advanced Composite Materials

The third and final class of materials selected for review in this section on technical issues and R&D opportunities is the so-called advanced composite materials. This class of composite materials is usually intended to replace conventional structural alloys (aluminum, titanium, and steel) in weight critical applications. Similar to other forms of composite materials, advanced composite materials derive their superior properties by incorporating high strength/stiffness fibers in a ductile polymer matrix or a ductile metal matrix. Through

the composite behavior of the two constituents, high specific strength/stiffness materials are obtained with useful engineering ductility. Another advantage of composite materials in structural design optimization is their versatility in tailoring local material properties by varying reinforcement configuration and geometry. Although advanced composites offer significant weight savings over conventional structural alloys, economic and other issues have precluded their large-scale use in DoD systems. As previously discussed, however, significant uses of advanced composites are planned for future Naval aircraft, and it is anticipated that other major system applications will follow.

A partial listing of the fiber-matrix pairs available for advanced organic matrix composites is given in Table II. The two most common types of matrix materials are the polyester and epoxy systems. Based on its strength and moisture resistant properties, the epoxy matrix is a leading candidate for high performance Naval applications. The polyimide, phenolic, and thermoplastic materials are of increasing interest for composite matrices because of their enhanced thermal stability. However, these systems are usually difficult to process. A promising matrix material for V/STOL applications is the NRL-developed phthalocyanines.[20] The potential attributes of this system are long-term thermal stability above 200°C, insensitivity to moisture and ease of fabrication. Of the various fiber reinforcements available, glass is used in the largest volume. The recently developed Du Pont polybenzamide fiber, Kevlar, has received increased usage because of higher modulus, lower density and lower cost than glass fibers. Currently, the graphite fiber is the leading reinforcement of organic matrix composites for military aircraft structures and skins.

TABLE II
Organic Matrix Composites

Fiber	Matrix Materials (Organic Polymers)
Graphic	Polyesters
Boron	Epoxies
S Glass	Phenolics
E Glass	Polyimides
Silicon Carbide	Phthalocyanines
Kevlar	Polycarbonates
	Thermoplastics

The superior specific strength properties of organic matrix composites relative to conventional structural alloys are shown in Figure 11. The two to four fold improvements shown in Figure 11 are indicative of the weight saving projected in Figure 2 for V/STOL applications. Graphite/epoxy is the designated advanced composite material for the F-18 and the AV-8B aircrafts.

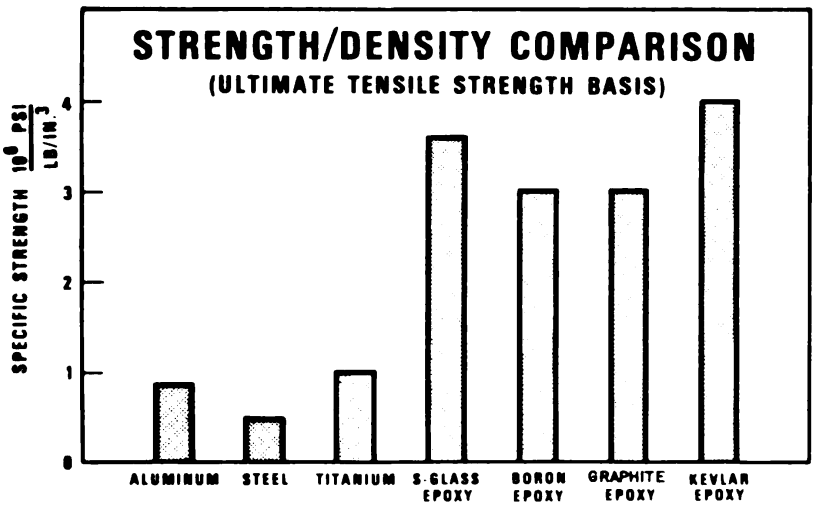

Figure 11 Comparison of specific strengths of advanced organic composites and structural alloys.

Although organic matrix composites provide significant structural efficiency advantages and are cost competitive, several technical issues cloud the extent of their future utilization. One remaining problem concerns the chemical characterization and quality control aspects of organic matrix composites through the production pipeline. The property-processing relationships of these composites are sensitive to slight changes in chemical composition of the constituents. In response to this problem, a coordinated effort has been instituted by the R&D community of DoD and other users to develop quality assurance techniques. Other technical issues facing organic matrix composites utilization include long-term moisture effects, nondestructive inspection, electromagnetic shielding, and field repair.

In comparison to organic systems, the developmental support of metal matrix composites has been at a low level of effort. One reason for the curtailed investment in and use of metal matrix composites is their high acquisition costs ($/lb.). Although an increase in production volume would significantly lower the cost of metal matrix composites, it does not appear that the required mass market will be

generated in the near future. From the Naval applications perspective, however, their high acquisition cost is not a sufficient criterion for curtailing their continued development. As was previously noted, life cycle costs are usually more significant for Naval systems than materials acquisition or fabrication costs. Moreover, for high value systems, improvements in performance, availability, and damage tolerance can justify high materials acquisition costs. Because of their embryonic state of development, it is not always possible to develop cost versus system benefit relationships for metal matrix composites. Nonetheless, the unique properties and potential options offered by metal matrix composites demand their continual development. For example, these materials could impact known as well as unforeseen requirements brought about by the inadequacy of current materials properties, raw materials and energy shortages, environmental/safety restrictions, and future threats.

Some of the more promising fiber-matrix pairs which have been processed into advanced composites are listed in Table III. Because of processing compatibility requirements, the fiber and matrix metal are not as interchangeable as the organic composite constituents. One intrinsic advantage of metal matrix systems over their organic counterpart is enhanced property retention at elevated temperature. This advantage is shown in the projected relative weight (at constant compression stress) versus temperature relationships of Figure 12.[21] The three leading metal matrix candidates – boron/aluminum, aluminum-oxide/aluminum and graphite/aluminum are seen to extend well beyond the temperature limits of the epoxy matrix composites and are more efficient than titanium or the more thermally stable resin matrix materials in the 200 to 400°C temperature range. For higher temperatures, the refractory wire/superalloys and ceramic/superalloys discussed in the previous section on thermostructural materials are applicable.

The projections of Figure 12 lead to the obvious suggestion that advanced metal matrix composites be developed for applications in the temperature range 200-400°C, that is complementary to the organic matrix composites and thermostructural materials. These applications include fan blades, frame and ducts of propulsion systems; aircraft and missile structures in close proximity to engine exhaust; lightweight gun barrels; and rocket motor cases. The results shown in Figure 12 also suggests that metal matrix composites be considered as a replacement for titanium alloys in weight critical applications, e.g., aircraft primary structures and control surfaces. Boron/aluminum composite is used extensively in a primary truss structure of the NASA space shuttle. Because of their high tempera-

TABLE III
Metal Matrix Composites

Fiber	Matrix
Boron	Aluminum Titanium
Graphite	Aluminum
Silicon Carbide	Aluminum
Alumina (Al_2O_3)	Aluminum Magnesium

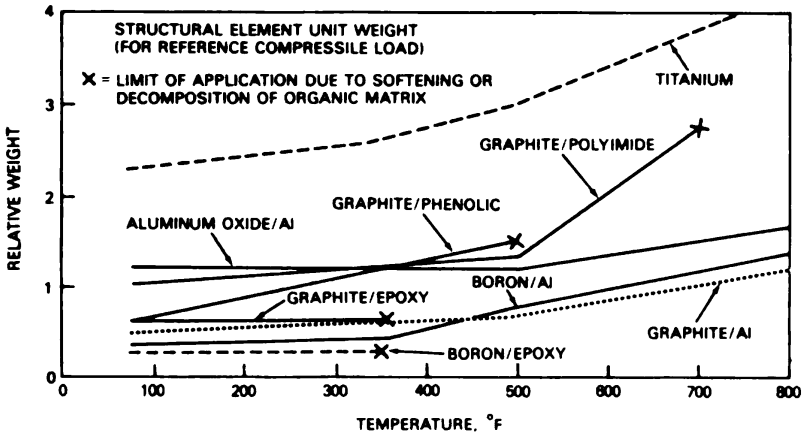

Figure 12 – Advanced composites performance potential (projected 1980)–Relative materials weight versus maximum service temperature (Ref. 21).

ture capabilities, metal matrix composites are also candidates as lightweight structural material with improved fire resistance properties. In addition, these materials have an undefined potential as lightweight armor.

To realize the material options offered by both metal matrix and organic matrix composites, however, will require a comprehensive development approach, analogous to those defined for high strength marine alloy and thermostructural materials. The elements of this approach include: (1) obtain optimum balance of required properties and performance parameters, (2) develop consistent characterization, design, and inspection criteria, (3) generate adequate data base of critical properties and service environment effects, (4) evolve rapid, cost effective fabrication and repair techniques.

Also, implicit in this development approach is the innovative design of component and structures in such a way as to take full advantage of composite construction rather than the direct substitution in conventional alloy designs.

Summary Statement

In this article, an attempt has been made to illustrate the complexity and diversity of the challenges facing the Navy's structural materials community over the next several decades. In order to limit the article to a tractable length, however, it was not feasible to provide a more comprehensive review. Reluctantly, many important requirements, issues and opportunities were omitted, including those for strategic missile structures, space system structures and submarines. These topics are prime candidates for other review articles, and a priority of efforts should not be inferred by their omission herein.

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Real-Time Analysis in Chemical Oceanography

Alberto Zirino, Cesar Clavell, Jr. and Peter F. Seligman*
Naval Ocean Systems

Introduction

In the past the Navy's interest in the chemistry of seawater has focused on problems of corrosion and as a service in support of the study of physical oceanography, which has provided acoustic and physical information essential to naval operations. Only recently has the need to understand biochemical processes in the sea also been recognized. This need occurs chiefly in the areas of environmental protection and acoustic prediction.

The Office of Naval Research and the Naval Facilities Engineering Command have supported at the Naval Ocean Systems Center (NOSC), San Diego, a chemistry and environmental sciences group charged with conducting research and development in those areas which would expedite the Navy's task of environmental assessment. The primary objective of this task is a better understanding of the effects of the Navy's operations on inshore and nearshore environments and ecosystems. As a part of NOSC's environmental assessment program, this paper attempts to trace the role of analytical chemistry in shaping the field of chemical oceanography. It suggests that our understanding of complex physico-biochemical processes is limited by our analytical capabilities. Additionally, it describes the operation of newly developed systems which incorporate minicomputers and microprocessors for real time measurement of trace metals and other chemical variables. Eventually, the automated techniques used in these systems may be adapted for real-time measurement of micro-organisms in the water.

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Background

Historical Constraints

The words chemical oceanography invoke visions of tennis-shoed chemists on white ships gliding smoothly across glistening blue and white waves in pursuit of mysterious chemical trails. The words, of course, do mean "chemical mapping of the ocean" and in the past came to describe the investigation of marine phenomena of a physical, geological, or biological nature by charting chemical variables. Although little new chemical information was produced, the field of chemistry, particularly the analytical methodology, was heavily tapped for those aspects which could be transferred to the study of the sea.

Physical problems, those concerned with the distribution of the density of seawater, yielded readily to analytical investigations, and many chemical contributions to physical oceanography were made early in the history of the field. Predictably, the sea did not give up secrets of its life processes as easily, for those substances which are of greatest biological interest are found in seawater at parts-per-billion concentrations, mixed with a millionfold excess of sea salt. For this reason, state-of-the-art analytical chemistry often proved to be deficient in sensitivity. Moreover, it was frequently totally unworkable at sea, where salt spray, pitching decks, and wavering bulkheads caused instruments to rust, liquids to spill, and glassware to shatter.

Investigation of biological processes was sometimes delayed because no appropriate analytical method existed. For example, although K. Brant suggested toward the end of the nineteenth century that a direct relationship existed between the availability of dissolved nutrients and oceanic productivity, he was unable to confirm his hypothesis because routine methods for the determination of phosphate and nitrate in seawater were not available. However, by the early 1920s techniques for the analysis of these trace nutrients and of dissolved gases were well established, and a basic understanding of the chemical fluxes which accompany life processes followed. Plate yields (primary production), nutrients, oxygen, and carbon dioxide were placed in a theoretical framework which is still the basic tenet of chemical oceanography.

Routine, open ocean, analytical chemistry was established by H. Wattenberg aboard the German research vessel *Meteor*, and his observations in the South Atlantic Ocean (1925–1931) illustrated the dynamic aspects of chemical oceanography. Chemical variables were

treated as functions of time and space, and the information obtainable from an oceanic area was recognized as being dependent upon the oceanographers' ability to carry out rapid, precise, and accurate chemical analyses under adverse laboratory conditions. Resolution of these variables over time and distance became the primary goal of sea-going chemistry.

The limitations to the resolution were not purely analytical, of course. Time is a significant factor, particularly in sampling. A single ship cannot sample two locations simultaneously. Resolution may be limited by the time required to move from one station to another. If a single station is occupied, the resolution depends on the time required to repeat an analysis. If a new set of sampling bottles must be lowered for each chemical determination, the resolution in time for deep samples will be several hours at least. During this period the ship and the water will have moved under the influence of winds, currents, and surface and internal waves.

An additional factor is the very small volume of water that can be analyzed compared to the volume of water sampled. In general, samples are collected with water bottles of finite volume like that shown in Figure 1. Always, *a priori* decisions must be made as to which water is to be collected and which is to be excluded. Because the sample volume is small, relatively large volumes of water must be excluded. Nevertheless, linear gradients are always drawn between sampled points even though they are over vast depths and distances. This limits the accuracy of the values recorded for most of the volume sampled.

Ultimately, when all of the compromises have been made and resolution has been optimized, the ability to discriminate lies within the precision and accuracy of the analysis. Even in this, the chemical oceanographer's task is more difficult than that of his land-bound colleagues. The sample can be contaminated by the rusting hull of the ship, by the sample bottles, or by the wire used to lower them. Trace substances to be analyzed can be removed from the seawater by adsorption on container walls, or, in case of gases, by exchange with the atmosphere. If the sample manages to reach the ship's laboratory unaltered, minor difficulties such as the reading of a see-sawing meniscus or an electrically noisy power supply will introduce error. Finally, many sea-going chemists do not feel very well on a moving platform and find that simple chemical analyses become difficult when performed at sea, while difficult ones become impossible.

However, to simply dwell on the difficulties of performing chemical measurements in oceanographic research is misleading. The important point is that the constraints imposed by having to sample

Figure 1 – The traditional method of sampling by bottle limits the resolution with which chemical variables can be measured in the ocean.

a nearly infinite environment in finite time, and the limitations to resolution imposed by the analytical methods established the boundaries within which the science of chemical oceanography has developed. Problems which lent themselves to steady state solution or to interpretations of thermo-dynamic equilibrium were accessible. Geochemical problems are, of course, most amenable to this treatment, and the first edition of *Chemical Oceanography*, a multi-author, comprehensive work published in 1965, has a distinctly geologic flavor. Not only are 9 of the 19 authors geologists, but the individual chapters and topics are presented as so many minerals to be studied, e.g., Carbon Dioxide, Silicon, Minor Elements, Major Elements, and so on. With the exception of Strickland's chapter on marine productivity, the dynamic processes presented are geological:

carbonate precipitation, oceanic salt deposition and metamorphism, and formation of marine sedimentary iron ores. Marine biochemistry is portrayed as a static science. Trace nutrients and dissolved organic matter are simply presented by concentration vs. depth profiles at selected locations. Quantitative relationships between nutrients, organic matter, and oxygen are drawn without regard to rates. There is only a single hint of the dynamic character of biological-chemical oceanography – Strickland's compartment diagram of an idealized food web, in which the magnitudes of fluxes between compartments are denoted by arrows of varying thickness.

Interestingly, the publication of the first edition of *Chemical Oceanography* also marked the end of an era. There was marked dissatisfaction among investigators with routine analytical determinations and simple stoichiometric relationships. During the last decade, a new generation of scientists trained primarily in physical chemistry began to unravel established problems with a new degree of mathematical sophistication. The very name "chemical oceanography" was neglected by nearly all in favor of "marine chemistry," which denoted less of surveys and more of serious, introspective laboratory investigations. Equilibrium chemistry was applied rigorously to oceanographic problems, particularly to the study of the major components of sea salts. Some marine chemists discovered that careful experiments were best conducted in a shore-based laboratory and that it was not necessary to go to sea. Others found that mathematical models could be constructed on computers without even resorting to the laboratory, and models proliferated. Marine chemistry came of age in 1975 with the publication of the second edition of *Chemical Oceanography*, now expanded from two to six volumes. Marine physical chemistry is prominent in this edition, which includes such articles as Seawater as an Electrolyte Solution, Chemical Speciation, and Adsorption. The basic article on CO_2 now includes discussions of partial molal volumes, as well as expanded presentations on rates of CO_2 exchange and compartment models. Analytical methods require two articles, one on the electroanalytical chemistry of seawater, and a second which dwells on other methods.

Recent Developments

Despite the increase in chemical and mathematical erudition with which oceanic processes have been viewed recently, the basic geologic approach to the chemistry of the oceans still prevails. This is due primarily to analytical limitations to the study of chemical changes associated with rapidly occurring biological processes. At

present, only a few of those substances which initiate, support, regulate, and serve as indicators of primary production are measurable in the field with sufficient accuracy and rapidity to provide adequate information. We do not have real time or near real time methods for measuring most trace substances required by marine plants (i.e., vitamins, metals, and organic metal chelators) and for analyzing the products of plant metabolism and decomposition (i.e., carbohydrates and other unspecified dissolved hydrocarbons, amino acids and polypeptides, humic and fatty acids, nucleic acids, antibiotics, etc.).

There are at present rapid, automated analyses for nitrates, phosphates, and other inorganic constituents in the water. These methods, based on calorimetric determinations of flowing, bubble-segmented solutions, are now part of standard shipboard procedure and have been used in the study of upwelling processes and internal waves. Nevertheless, these advances mark only the beginning of the analytical effort required to understand the complex marine chemical-physical-biological interactions. A new level of sophistication permitting real-time analysis is required. Fortunately, a revolution occurring in analytical chemistry promises to supply the shipboard methodology for the more difficult assays and may change the course of traditional chemical oceanography. In the new chemical oceanography, sophisticated instrumentation is taken to sea to provide data of sufficient resolution to substantially increase our understanding of biological events.

Real-Time Analysis

The important development in analytical methodology is of course the addition of minicomputers and microprocessors to chemical sensors to form "intelligent" chemical instruments. These instruments, under control of their own internal computers, can collect samples, add reagents, mix, shake, atomize, or otherwise treat the sample as prescribed by the analysis, read the sensor output, add standards, repeat the procedure, and operate on the data to produce the desired information in the proper units. Already marketed is a gas chromatograph in which the microprocessor controls every event, from turning on the oven to injecting the samples. The unit also prints out a complete analytical report. Similarly, there now exists an atomic absorption unit in which the spectrophotometer automatically recalibrates itself and finds the most intense absorption peak near a predesignated wavelength.

Although these instruments have been designed as laboratory units, it is not difficult to envision an oceanographic ship fully loaded with automated instrumentation which unerringly performs sophisticated chemical analyses while the vessel is on station or in transit. Indeed, automated analyses (and experiments) and data reduction mean progress in chemical oceanography.

Flow-Through Systems

Certain features peculiar to marine chemical analyses deserve mention. Sampling can be done by lowering an instrument into the sea or by bringing a sample aboard the ship through some noncontaminating pumping system. Both approaches are being researched, and both have limitations. At NOSC the latter approach was adopted because it was felt that the difficulties associated with the construction of pressure-resistant, watertight instrumentation would interfere with the basic effort to design equipment for highly complex automated analyses. Additionally, a large number of sophisticated, automated analyses could be carried out simultaneously in a ship's laboratory, while an *in-situ* instrument would be limited by size and other physical constraints.

A second feature of note is that tubular sensors can be adapted into the sampling stream more easily than sensors of different design. Thus, an instrument with sensors in the tubular configuration can be placed "on line" and tap into a continuous source of seawater. If discrete samples are also desired, they can be collected in "loops" which access the mainstream through solenoid-operated valves.

The concepts of underway sampling and automated instrumentation are illustrated by the automated trace metal analyzer developed at NOSC. The unit analyzes Zn, Cu, Pb and Cd in seawater by means of an electrochemical technique known as anodic stripping voltammetry (ASV). In this process, metals in seawater are amalgamated at constant potential with a thin Hg film which is itself plated inside of a graphite tube. Metals are accumulated and concentrated in the film for several minutes, then rapidly released by decreasing the applied potential. The diffusion of metals out of the film can be measured as a series of current "peaks" on a strip chart recorder. The technique is extremely sensitive; and because it requires few chemical reagents, it is relatively free of contamination. The NOSC unit, which is controlled by a specially designed programmer, consists of an electrolysis cell, a potentiostat and a recorder. Its operation is illustrated in Figure 2. The cell contains a sampling pump which collects seawater through a plastic hose, as well as a

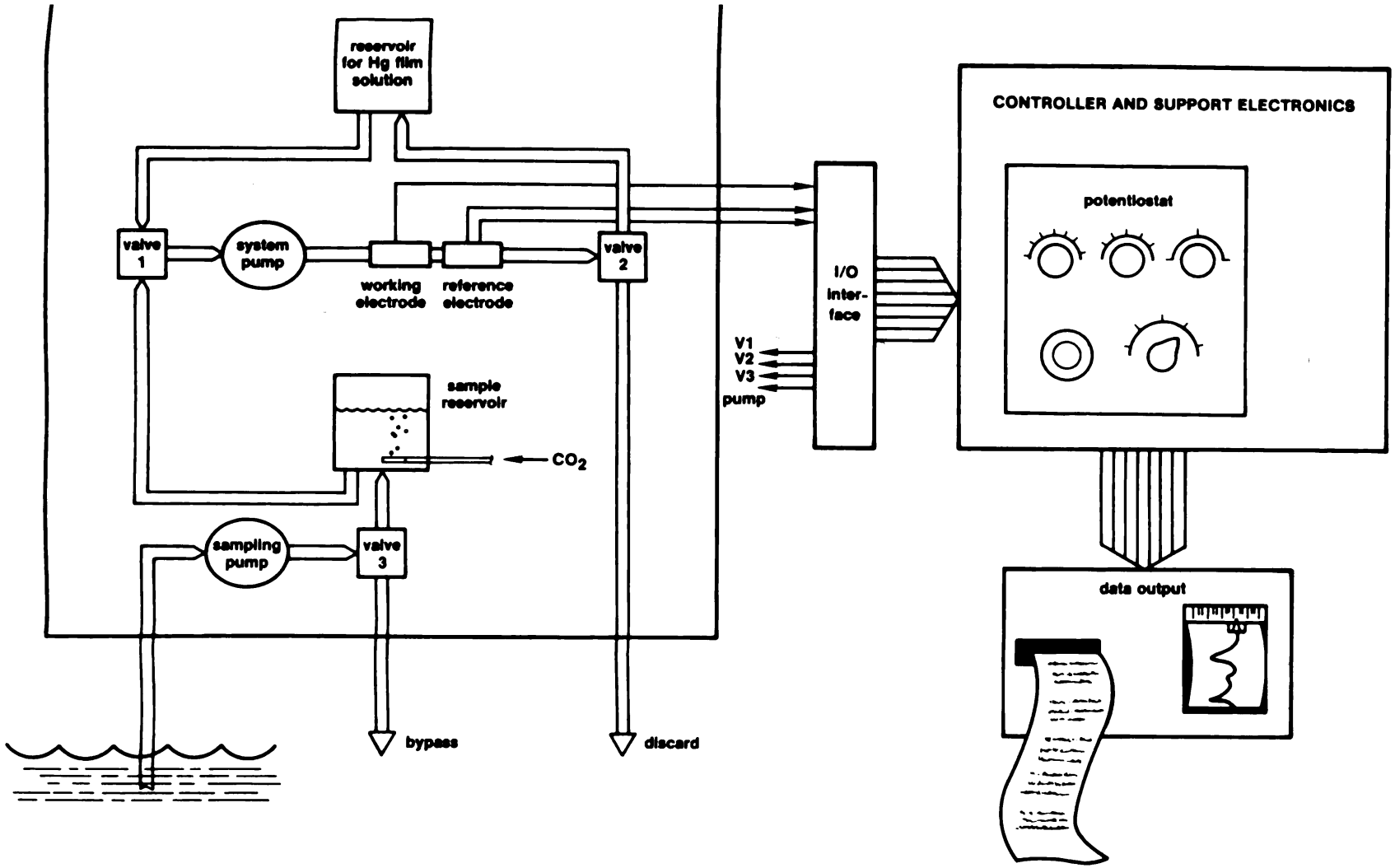

Figure 2 – A flow-through anodic stripping voltammetry system was developed at NOSC for automated sampling and analysis of trace metals in seawater.

recirculating pump and three solenoid-operated valves which sequentially collect a sample and recirculate it through a set of tubular electrodes, purge the sample of oxygen with CO_2, coat the electrode with Hg, concentrate metals in the Hg film, and complete the analysis. A third pump adds a standard every third sample against which measurements are made.

This automated ASV system has been used to measure trace metals from a small vessel in Southern California coastal waters, in Pearl Harbor, in San Diego Bay, and in the Peruvian upwelling area. When Zn was measured at a stationary pier location at Pt. Loma, in San Diego Bay, it was observed that the Zn concentration fluctuated regularly with the tidal period. Figure 3 shows this relationship. This was attributed to the fact that relatively metal-free open-ocean water moved into the bay and past the intake at flood tide, while relatively polluted bay water was sampled at the inlet during low tide. Cu, measured at the same location, fluctuated similarly. This experiment is notable because conventional single measurements made using sampling bottles at this location would not have shown these rapid fluctuations in concentration. Erroneous conclusions could have been reached regarding the concentration of these trace metals in San Diego Bay.

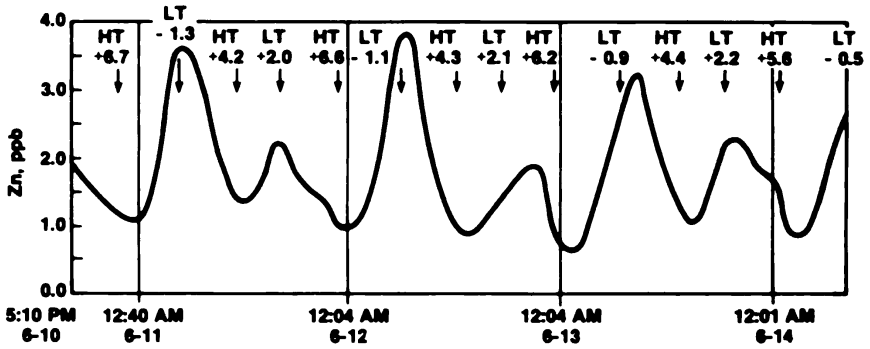

Figure 3 – Fluctuations of Zn concentration with tidal period in San Diego Bay. HT and LT denote high and low tides from the 10th to the 14th of June.

Biochemical Oceanography

Similarly, when surface pH, temperature, and chlorophyll-a fluorescence (an indicator of the plant crop) were measured while underway aboard a small vessel which was passing the discharge of a thermoelectric plant in the east loch of Pearl Harbor, distinct changes were noted which might have been missed by conventional sampling (Figure 4). For example, the higher acidity of the discharged water is

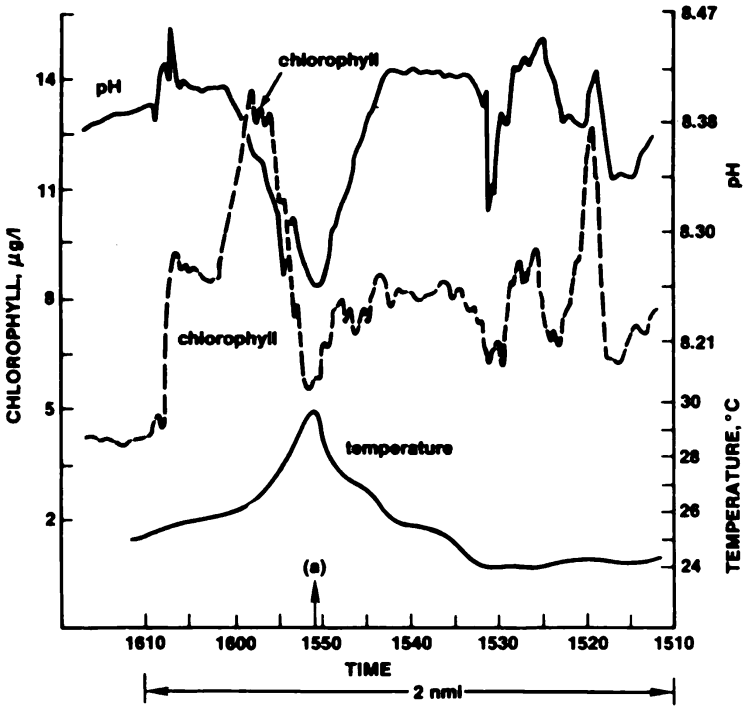

Figure 4 – Continuous measurement of chlorophyll-a, pH and temperature in the surface waters of Pearl Harbor, Hawaii, east loch. Measurement is west to east, past the discharge of a thermoelectric plant (a). January 10, 1977. (Courtesy of Mr. Robert Darwin, Navy Material Command.)

clearly detectable in the pH, which decreases rapidly from an ambient 8.4 to 8.3. West of the discharge the fine structure in the pH profile clearly matches the detail in the chlorophyll-a profile. This occurs because the plankton removes CO_2 from the water during photosynthesis and raises the ambient pH. Similarly, the absence of an increase in pH corresponding to the large phytoplankton patch east of the power plant suggests that photosynthesis may have been depressed by the extraneous warm water. These and similar observations made by us in coastal and oceanic waters point out the considerable degree of variability associated with biologically active areas.

The interrelationship noted between chlorophyll-a and pH suggests that real-time measurement of chemical constituents must ultimately be matched with a parallel real-time measurement of the organisms in the water. Those organisms most sensitive to chemical changes in the water and which lend themselves to an instrumented analysis are the microalgae or phytoplankton. An organism of this type is shown in Figure 5. These plants are separated from the water only by a semipermeable membrane (the cell wall), and during their lifetime chemicals are exchanged readily through the membrane by

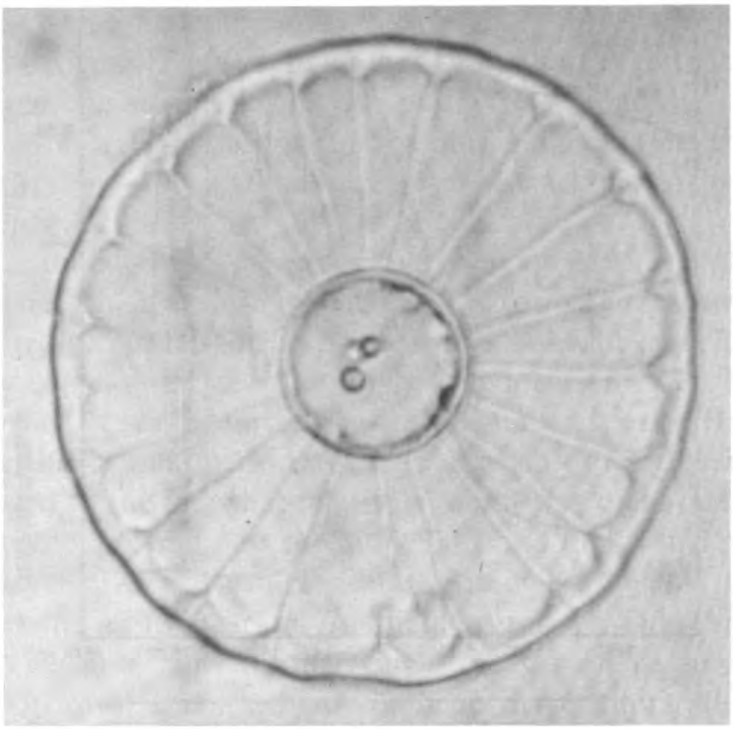

Figure 5 – Phytoplankton can serve as environmental sensors because their semipermeable cell walls make them sensitive to chemical changes in the surrounding seawater. Variations in the phytoplanktons' rates of reproduction signal chemical changes in the environment; these can be detected using automated sampling techniques.

diffusion and various processes of uptake and excretion. The phytoplankton respond to environmental changes by altering their rates of division and reproduction. These alterations are reflected in the field by changes in the species composition and in the population densities. Real-time measurement of the phytoplankton can provide very valuable information on the state of the marine environment. Indeed, no valid environmental assessment can be based on purely chemical data, since substances are toxic, neutral, or beneficial only with respect to living beings.

Fluorometry appears to be a promising tool for studying population diversity as well. Phytoplankton population densities are already being estimated by the *in vivo* measurement of the fluorescence of chlorophyll-a at 685 nm after excitation at 436 nm. If the wavelength of the excitation source is varied, say from between 350 and 650 nm, the resulting fluorescence at 685 nm varies in intensity to give a pattern with enough structure and detail to be useful for the characterization of plankton to the genus level. Figure 6 presents an

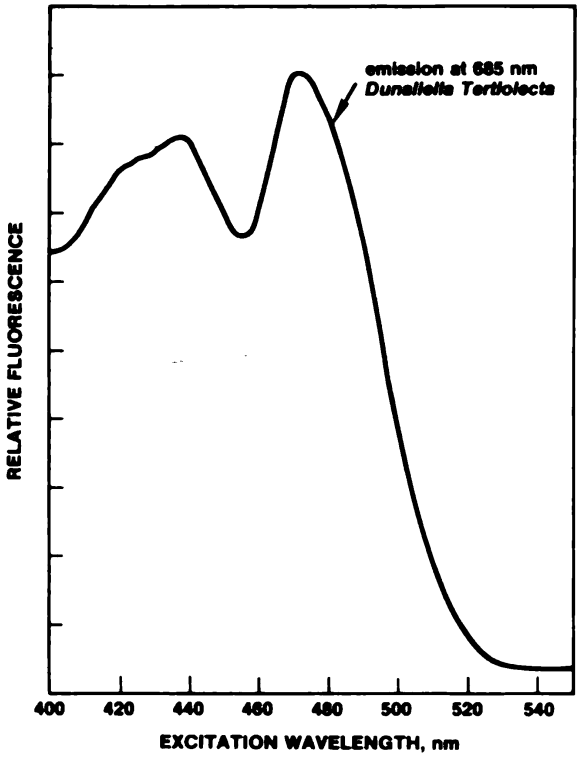

Figure 6 – Chlorophyll-a fluorescence may prove useful in identifying phytoplankton. Varying the wavelength of the excitation source produces a characteristic pattern of fluorescence.

example. Additionally, for a particular group of organisms, there exists the possibility that variations in the intensity of fluorescence may be used to assess the physiological condition. Needless to say, a workable shipboard or towed *in-situ* fluorometer would quickly accumulate an inordinate amount of data both from the organisms and from the water. However, the handling of these data is not a problem on modern oceanographic ships which contain their own computer centers. Indeed, it is not too difficult to envision entire computer-controlled sea-going laboratories making chemical and biological measurements in or near real-time. It is fully expected that the newly evolving technology will introduce the chemical oceanographer to the dynamic aspects of his science which have eluded him in the past.

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Satellite Observations Help Explain Oceanic Behavior

Satellite photographs have revealed oceanographic features that might otherwise have been missed by more conventional oceanographic observations as, for example, the large scale eddies eminating from the Gulf Stream as it flows through the Atlantic Ocean. But turning to another part of the oceanic scene, satellite images of the coastal regions of the world's oceans have also revealed the ubiquitous presence of internal solitary waves that are apparently generated by tidal flows at the edge of the Continental Shelf and which then evolve, propagate and interact in certain distinctive ways. Through a series of laboratory hydrodynamic experiments, Professor Anthony Maxworthy of University of Southern California, supported by the Office of Naval Research, has postulated an explanation for some parts of the observations. In particular, as an ebb tide flows at the Shelf edge, in the presence of a well defined mixed layer and when a critical Froude number is reached, a depression is formed in the mixed layer that propagates shoreward as the tide slackens. The depression steepens but is unable to maintain its shape and it evolves into a sequence of solitary waves, the number and magnitude of which depend on the exact shape of the depression and the stratification. These waves are ordered by amplitude, with the largest, fastest first. Available theory is able to explain most of the features of these waves satisfactorily. As waves from different sources interact a resonant condition can be reached at a critical value of the angle between them and a third wave created. This type of interaction can also be described theoretically and has been observed in experiments and is clear in many of the satellite observations. Field observations are or will be made to validate Maxworthy's experimental results.

Research Notes

Turbomachine Aeroelasticity Research

Some of the results of the Office of Naval Research supported study on aerodynamically induced vibrations of axial flow compressor blades conducted by Professor Fred Sisto are described here. This work is concerned with the development of a rational understanding of why these airfoils, particularly those attached to rotors, are subject to self excited vibrations known as flutter. The type of flutter most commonly encountered in the compressor and fan components of jet engines occurs at conditions of ground startup and also, unfortunately, at very high flight speed. When operating at these conditions, the angle of attack of the blades in the front stages tends to be larger than at design point operation; and therefore stalling or breakaway of the flow from the airfoil suction surfaces is prone to occur. Hence the term stall flutter is applied to this troublesome and potentially destructive phenomenon.

The major difficulty with understanding and attempting to predict stall flutter occurence is the fact that stalled, or separated, flow is not amenable to analysis. This situation prior to Professor Sisto's reassessment of the turbomachine stall flutter problem had to led to a more or less totally empirical method of procedure. Either a new compressor design would be subjected to extensive experimental flutter evaluation in the pre-production development phase, or else an exhaustive experimental cataloging of the stall flutter behavior of a large number of parametrically related single compressor stages was required before the compressor was designed. The former delayed possible corrective procedure to a late epoch in the development cycle; the latter was a brute force approach of enormous proportions.

The new feature which was brought to the stall-flutter prediction algorithm was an attempt to reduce the problem to semi-empiricism. If separate means were available for predicting the location and movement of the separation streamline on the suction side of each airfoil, a reasonably accurate calculation of the nonsteady lift and moment acting on the airfoil could be generated by suitable nonsteady aerodynamic analysis.

In a series of theoretical studies the graduate students at Stevens have formulated the reactions experienced by a single airfoil, and later a cascade of airfoils, with specified vibratory motion and with specified periodic motion of the separation point. Results of these studies have appeared in a series of journal papers and thesis documents. Specific information has been gathered utilizing experimental apparatus concerning the parameters which affect stall flutter and the related phenomenon of forced vibration as well. However, the measurement of separation point behavior has been only partially successful, and then only by inferential means.

One set of such experiments has involved the slow oscillatory displacements of every airfoil in an annular cascade wind tunnel. When oscillated in a torsional mode, with fixed interblade phase angle, the measured aerodynamic moment about the torsion center exhibits sudden departures from linear behavior. Each such departure (stalling) is attributable to separation point migration along the suction surface of the blade or airfoil. Certain combinations of mean angle of attack, torsional amplitude, interblade phase angle and

cascade geometry lead to sufficient departures from linearity such that the work done by the aerodynamic moment on the twisting displacement changes sign. The locus of points of zero work defines the flutter boundary in whatever coordinates are chosen for the representation.

The main shortcoming with the experiments described above is in the very long period of the forced oscillatory motion of the apparatus. In practice stall flutter occurs at frequencies of hundreds of hertz and up into the kilohertz range. Nevertheless, there is qualitative correlation between the zero work "flutter boundary" and the results of actual free flutter tests which may be obtained in the same apparatus by spring mounting the individual blades and disconnecting the forced oscillation driver.

In order to obtain a clearer definition of possible separation point behavior some extensively instrumented tests were performed at United Technologies Researh Center and sponsored by ONR and the Air Force Office of Scientific Research. The tests in this coordiated research program used a very large scale linear oscillating cascade of airfoils instrumented with hot film gages and surface-mounted pressure transducers. Both gages and transducers had very high frequency responses.

Preliminary reduction and interpretation of that data has proved to be difficult; it was not possible to establish with certitude that a separation emanated from a point on the blade suction surface and moved periodically with the period of the forced oscillation. Hence direct confirmation of the "moving separation point" theory remains to be confirmed as an element in the semi-empirical treatment of stall flutter.

However, in those experiments at United Technologies Research Center performed by F. Carta for helicopter applications, there seemed to be an interpretation of some of the data that would indicate the possibility of a different type of separation phenomenon under some conditions. The flow may in fact separate from or near the leading edge at high angles of attack and then *reattach* to the sunction surface creating a bubble of low velocity (and hence low perturbation pressure) fluid near the nose of the profile. This behavior might be expected for example with highly staggered airfoils having small leading edge radii. If the reattachment point then varied periodically with time, a different instability mechanism would be available for explaining stall flutter, and the focus then shifts to establishing the semi-empiricism of reattachment point behavior.

Along with the construction of a new research compressor to attempt experimental determination of separated flow behavior, by laser doppler anemometry, the theoretical aspects of unsteady leading edge bubble aerodynamics are being pursued by the current group at Stevens Institute.

A Data Base Computer

ONR contractor David Hsiao, of Ohio State University, has spent the last several years doing pioneering work in data base designs. He began his work by developing the "security atom concept" which provides theoretically sound, selective control of users access to computer stored data at the file, record, data element, and value level. Then Professor Hsiao studied hardware structures optimized for particular task of data base access. Instead of serially accessing

data from a disk, Hsiao's mass storage device includes the idea of a small processor on each track of the recording surface, resulting in the capability of searching enormous amounts of data simultaneously. Hsiao then developed a series of abstract models of components and data structures optimized for computer access and management of data structures, and demonstrated how these functions simultaneous operating processing modules, each optimized for its task. Finally, Hsiao has shown both analytically and through simulation that his data base computer is general enough to meet all the requirements of relational, hierarchical, and network data bases, and has even developed a high level language for the specification of security requirements including several levels of specification depending on the sophistication of the user.

To appreciate Hsiao's contribution, one should be aware of the fact that current data bases and security features are implemented in conventional general purpose systems. Data search and retrieval algorithms are programmed in a high level language, and executed in a serial manner. Data is stored on serial access devices, and data security features are added-on software packages sharing the same general purpose hardware as the search and retrieval functions. It has been apparent for some time that Defense command, control, communication, and intelligence system requirements for increasingly large, efficient, and secure data bases cannot be met by existing computer systems.

To facilitate the ultimate development of Hsiao's security concepts, ONR has put together an evaluation and prototype design team consisting of representatives from the original Ohio State University research group, Univac Corp., and other qualified academicians. To the extent that a scheduled one year design evaluation phase yields positive results, Univac (with Ohio State's involvement) will move forward to the construction of a prototype Data Base Computer. Of additional interest here is the funding arrangement; ONR will continue to underwrite the participation of Ohio State researchers — Univac, demonstrating its enthusiasm for the basic design, will pay its own way including budgets for personnel and construction of the prototype computer. Success in this effort will make an important contribution to Navy, and indeed, national needs for very large, secure, efficient data base storage and retrieval systems.

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Cover Caption

Naval Ocean Systems Center scientists carry out real-time biological and chemical measurements in San Diego Bay using instrumented survey boat. *(See page 26.)*

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