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FUTURE RESEARCH DIRECTIONS TO UNDERSTANDING FACTORS INFLUENCING ADVANCED HIGH TEMPERATURE MATERIALS

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ABSTRACT

High temperature applications demand materials that have a variety of properties such as high strength, toughness, creep resistance, fatigue resistance, as well as resistance to degradation by their interaction with the environment. All potential metallic materials are unstable in many high temperatures environments without the presence of a protective coating on the component surface. High temperature alloys derive their resistance to degradation by forming and maintaining a continuous protective oxide surface layer that is slow-growing, very stable, and adherent.

Propulsion materials for both Naval aircraft and ship gas turbine engines are subjected to the corrosive environment of the sea to differing degrees. Increasing fuel efficiency and platform capabilities require higher operating temperatures that may lead to new degradation modes of coatings and materials. Fuel contaminants or the lack of contaminants from alternative synthetic fuels may also strongly influence coating and/or materials performance which, in turn, can adversely affect the life in these propulsion or auxiliary gas turbine engines. This paper will dwell on some past results of materials testing and offer some views on future directions into materials research in high temperature materials in aggressive environments that will lead to new advanced propulsion materials for the VAATE program.

Keywords: high temperature materials, superalloys, ceramic matrix composites, synthetic fuels, corrosion, oxidation, hot corrosion, CMAS attack, thermal barrier coatings, salt, environmental barrier coatings, turbines,

INTRODUCTION

High-temperature corrosion and oxidation occur in various military applications. Aircraft, ships, vehicles, weapon systems, and land-based facilities require power that may be supplied by boilers, diesel engines, gas turbines, or any combination of the three power sources. High temperature exposure of materials occurs in many applications such as power plants (coal, oil, natural gas, and

nuclear), land-based gas turbine and diesel engines, gas turbine engines for aircraft, marine gas turbine engines for shipboard use, waste incineration, high-temperature fuel cells, and missile components. The service performances of boilers, diesels, and turbines can be affected by exposure to numerous environments and are affected by temperature, alloy or protective coating composition, time, and gas composition. Materials degradation can lead to problems that often bring about unscheduled outages resulting in loss of reliability, loss of readiness, decreased safety, and increased maintenance costs.

Predicting corrosion of metals and alloys or coated alloys is often difficult because of operational demands placed on a given power system, the range of the composition of corrosive gaseous or molten environments, and the variety of materials that may be used in a given power system. Moreover, corrosion prediction is further complicated because materials often degrade in a high-temperature environment by more than a single corrosion mechanism.

High Temperature Corrosion and Degradation Processes

There are a number of corrosion and degradation processes that may occur in boiler, diesel engines, gas turbine engines, and incinerators. The degree of degradation is dependent on the material being exposed and the specific environment and other conditions to which the material is exposed. High temperature corrosion/degradation of materials may occur through a number of potential processes [1] either singly and/or in some combination with one another:

- oxidation
- carburization and metal dusting
- sulfidation
- hot corrosion
- chloridation and other halogenization reactions
- hydrogen damage, hydrogen embrittlement
- molten salts
- aging reactions such as sensitization
- creep
- erosion/corrosion
- environmental cracking (stress corrosion cracking and corrosion fatigue)

Gas Turbine Engines

The gas turbine was developed generally for main propulsion and auxiliary power for aircraft, ships, or certain other military platforms that require a higher power density than diesel engines can generate. In the case of gas turbines, fuel and air quality, and the specific engine environment in which they operate influence the corrosion of turbine components significantly. Current gas turbines operate on the Brayton (constant pressure) cycle. A gas turbine has three major components: (1) compression of a gas (typically air), (2) addition of heat energy into the compressed gas by either directly firing or combusting the fuel in the compressed air or transferring the heat through a heat exchanger into the compressed gas followed by (3) expansion of the hot pressurized gases in a turbine to produce useful work [2]. The compressor is a series of blades or airfoils, some rotating (rotors), some stationary (stators) that draw air in and compresses it. The more rows of blades, the more the air pressure increases as it passes through the compressor stages. Typical pressures can be up to 40 times higher than atmospheric pressure.

There are several types of gas turbine engines. The primary purpose of aircraft gas turbines is to generate high performance and power quickly at the expense of fuel economy. Afterburning, or reheat, increases exhaust velocity and engine thrust for short times to improve aircraft take-off, climb, and

maneuverability by injecting additional fuel in the jet pipe. Vectored thrust engines employ swiveling nozzles that can direct the gas stream from vertically downward for upward lift through an arc to horizontally rearward for conventional forward thrust. Turbo shaft engines are used in helicopters, marine propulsion and auxiliary systems, and some land-based military assets. It uses a power turbine and a gearbox through which the power is transmitted directly to a variety of devices, such as the rotor system, ship or platform propulsion, or auxiliary systems.

Aero engines use relatively pure fuels with low sulfur contents and the air quality is generally good unless there are recurrent low altitude flights or operations over marine environments. Jet fuels JP-5 and JP-8 are petroleum-based and used as aircraft fuels by the military. JP-5 and JP-8 is shorthand for jet propellants 5 and 8. JP-5 is the U.S. Navy's primary jet fuel, and JP-8 is one of the jet fuels used by the other services.

Marine gas turbines in the U.S. Navy have had a long development process [3]. Shipboard marine gas turbines operate at lower metal temperatures (500-1000°C) than observed in aircraft gas turbines. Marine gas turbine engines serve as primary and auxiliary power sources for several current classes of ships in the U.S. Navy. It is desirable for marine gas turbine engines to have a mean time between removal of 20,000 hours.

High Temperature Processes

High temperature processes that may occur in aero gas turbines are dependent largely on environmental factors and the type of gas turbine engine. High temperature processes in aircraft gas turbine engines are generally due to high temperature oxidation or to high temperature creep. Thermal barrier coatings are being used to protect hot section alloys from catastrophic oxidation. Strict compositional control of the alloys is used in the hot sections of aero gas turbine which are either directionally solidified or are single crystals to improve the creep strength and prolong blade life from creep damage. High temperature corrosion at operating temperature does not occur often, but ingestion of sea salt in naval aircraft may result in pitting and molten salt corrosion if not water-washed often. Sand may cause abrasion of turbine components. The exposure to airborne dirt such as sand and ash may introduce silicates into the engine, commonly known as CMAS (CaO-MgO-Al₂O₃-SiO₂) which refers to the main chemical components of Ca, Mg, Al, and Si. Molten silicate deposits can penetrate thermal barrier coatings (TBCs) in advanced gas turbine engines due to increasing operating temperatures. Molten CMAS partially penetrates the TBC during the hot phase where the critical temperature is above 1240°C. Upon cooling the CMAS solidifies, reducing coating compliance, and promotes spallation of the infiltrated coating. Degradation appears to involve dissolution of the porous TBC columnar grains in the silicate melt and reprecipitation of dense globular zirconia crystals [4-6]. The yttria stabilizer is influenced by the silicate melt leading to the formation of monoclinic zirconia that is more prone to erosion damage and spallation. CMAS penetration can be substantially reduced by adding alumina, which lowers the melting point of the quaternary mixture.

Shipboard marine gas turbines operate at lower metal temperatures (500-1000°C) than observed in aircraft gas turbines; other degradation mechanisms are more observed in this temperature regime than is oxidation. While it is desirable for marine gas turbine engines to have a mean time between removal of 20,000 hours, several engines have fallen significantly short. The main reason for this shortfall is hot corrosion (Type I and Type II) damage in the hot section turbine hardware due to intrusion of salts from the marine air and/or from sulfur in the gas turbine combustion fuels. Historically, it has been shown that a condensed fused salt film is required for severe hot corrosion attack [7]. The attack does not depend on an alloy sulfidation-oxidation sequence, but on the development of a destructive fluxing action on the normally protective oxide which is dependent on the presence of Na₂O in the fused salt

films [8-10]. Thin films of Na_2CO_3 and NaNO_3 in contact with alloys produce accelerated attack similar to Na_2SO_4 , although sulfur is absent.

Experience in the 1960's and 1970's led to the discoveries of severe high temperature corrosion in shipboard gas turbine engines that usually did not occur in aircraft turbine engines. Early observations noted severe corrosion attack on the first stage blade and vane components of a shipboard marine gas turbine engine was sufficiently rapid to cause engine failure in several hundred hours [11]. The ingestion of sea salt and the combustion of fuels containing some measure of sulfur by gas turbine engines operating in marine environments can lead to corrosion of hot section components, particularly turbine vanes (nozzles) and blades (buckets). This attack was documented in the early open literature as hot corrosion as discussed earlier [12-14].

Besides acidic and basic fluxing reaction, hot corrosion is observed in marine gas turbines. Type I, high temperature hot corrosion (HTHC) occurs through basic fluxing and subsequent dissolution of the normally protective oxide scales by molten sulfate deposits that accumulate on the high-temperature component surfaces. A non-layer type corrosion characterized by smooth base alloy-oxide interface and continuous, uniform precipitate depleted zone containing discrete sulfide particles beneath the oxide scale is found [15]. HTHC usually occurs at metal temperatures ranging from 850 to 950 °C (1560-1740 °F). Type I hot corrosion involves general broad attack caused by internal sulfidation above 800 °C; alloy depletion is generally associated with the corrosion front. Basic fluxing attack involves raising the Na_2O activity in the molten sulfate by formation of metal sulfides [16]. Above approximately 950°C (1740°F), oxidation becomes the primary corrosion mechanism.

Type II, low temperature hot corrosion (LTHC) occurs in the temperature range of 650 to 750°C (1202-1382 °F) a layer-type corrosion characterized by uneven base alloy-oxide interface and the absence of subscale sulfides [15, 17]. Here the partial pressure p_{SO_3} is relatively high or melts are deficient in the oxide ion concentration leading to acidic fluxing of metal oxides that cause pitting from the formation of low melting mixtures of Na_2SO_4 and NiSO_4 or CoSO_4 in Ni-Cr, Co-Cr, Co-Cr-Al, and Ni-Cr-Al alloys.

Fuel and air quality, and the specific engine environment in which engines are operated, influence the observed corrosion of turbine components significantly. Other important factors that influence hot corrosion in gas turbines are composition of the gas, condensate composition and deposition rate, coating chemical and phase composition, coating quality, and temperature. U.S. Navy ships use as their primary fuel Marine Diesel, corresponding to NATO Specification F-76 or the U.S. equivalent, MIL-F-16884L [18] which recently reduced its maximum sulfur content from 1.0 wt% to 0.5 wt%. In addition, unfiltered air quality may contain up to 2600 ppm Na_2SO_4 , 19,000 ppm NaCl, and other seawater-derived species that further contributes to the environmental corrosive impact on materials in shipboard marine gas turbines. Filtration can reduce the NaCl content in air to ≤ 0.01 ppm, but this is still sufficient to generate Na_2SO_4 (as well as Na_2SO_4 directly created from sulfur in the fuel), which can lead to sulfidation and hot corrosion. Engine temperatures may also vary with operational loads by 400-500 °C when going from idle to full power [19]. The engine may also ingest solid particles (sand, ash, and dust) and pyrolytic carbon from poorly combusted or uncombusted conditions that contribute to metal loss via erosion or impact on turbine components. Carbon may accelerate corrosion by reducing sodium sulfate to sulfides [20].

When Naval fuels are unavailable and to minimize operational impact, commercial or Contract Marine Gas Oil (MGO) may be used to continue the mission of the ship(s). Navy Purchase Description (NPD) MGO fuel is subject to standard commercial practice quality control rather than the extensive handling and storage requirements specified for MIL-SPEC fuels. There have been several reports that use of MGO has increased hot corrosion of gas turbine components and that it has limited physical stability.

Occasionally, fuels may contain impurities such as vanadium, phosphorus, lead, chlorides, and unburned carbon, can be involved in lowering salt melting temperatures, altering the sulfate activity, or changing the solution chemistry and acidity/basicity that leads to accelerating sulfate hot corrosion. Yttria-stabilized zirconia (YSZ) is attacked at high temperatures and destabilized by phosphorus impurities in fuel [21]. The acid P_2O_5 reacts with basic Y_2O_3 to form the salt YPO_4 . Zirconia also synergistically reacts with sodium and P_2O_5 to form $NaZr_2(PO_4)_3$. The YSZ thermal barrier coatings (TBCs) have been exposed to $PbSO_4$ - Na_2SO_4 molten salts without observable destabilization or reaction with this ceramic [22]. However, lead, as PbO , appears to cause TBC failures by reacting with chromium in the NiCrAlY bond coat to form $PbCrO_4$.

The use of less refined, heavy fuels used in marine gas turbines may contain up to 200-ppm vanadium that when combined with Na_2SO_4 , accelerates hot corrosion reactions. The high-temperature reaction of sulfate and vanadium with ceramic oxides involved a Na_2O - V_2O_5 system that could be explained by Lewis acid-base chemistry [23]. Basic zirconia (ZrO_2)-stabilizing oxides, such as Y_2O_3 , do not react with Na_3VO_4 (or $3Na_2O$ - V_2O_5) but do react with the V_2O_5 component of $NaVO_3$ (Na_2O - V_2O_5) and V_2O_5 itself to form YVO_4 [24]. Acidic oxides, such as Ta_2O_5 , react with the Na_2O component of Na_2VO_4 and $NaVO_3$ to form sodium tantalates and yield α - $TaVO_5$ with V_2O_5 . The vanadate that is most corrosive in the initiation of vanadic attack will depend on the acidity/basicity of the coating or alloy oxide. No reaction occurs when the acid-base properties of a stabilizing oxide are equal [25]. The thermochemistry of vanadate and sulfate melts and reaction with different stabilizing oxides with SO_3 - $NaVO_3$ has been studied [26].

The engine may ingest solid particles (sand, ash, dust, and sea salt) and pyrolytic carbon from uncombusted or poor combustible conditions that contribute metal wastage by erosion or impact on turbine components. Thermal cycling or transient conditions may further increase the corrosivity of salt deposits by cracking protective oxide layers. The complexity of the turbine operating environment and other high temperature applications makes it nearly impossible to develop simple tests.

HOT SECTION MATERIAL BEHAVIOR

Marine gas turbines run cooler than aero engines; engine temperatures, until recently, have operated in the 500-1000°C range. For these temperatures, cobalt- or nickel based superalloys have been utilized as substrate materials for hot section blades and vanes. High-temperature alloy strength in marine gas turbines is not as critical as in aircraft engines, so alloys have tended to have multicrystalline and equiaxed microstructures [3]. In addition, for improved protection from hot corrosion, many alloys used in marine gas turbine have had a high Cr content.

High Temperature Coatings

High temperature coatings provide a barrier from corrosive or highly oxidative environments that may otherwise degrade the substrate alloy. To provide optimum performance coatings need to have good adherence to the substrate, ductility to resist thermal cycling, avoid defects that may provide easy pathways to deleterious gases, and maintain corrosion resistance over the design life of the high temperature component.

Aluminide diffusion coatings on transition metals and alloys such as iron, nickel and cobalt are β - $FeAl$, β - $NiAl$, and β - $CoAl$, respectively. Diffusion aluminide coatings are typically processed via pack cementation, slurry-diffusion or chemical vapor deposition [27]. Subsequent heat treatments help develop the proper mechanical properties and trigger further diffusion within the coating. The principal protective oxide is Al_2O_3 , which causes subsequent improved oxidation and corrosion resistance of aluminide coatings, although less protective oxides can form if other alloying elements are present in the substrate, either in solution or as precipitated phases [28]. Modified aluminide coatings are altered

by the addition of a secondary element like chromium, platinum, a reactive element, or a combination of these elements [27]. These coatings are generated by either: (1) incorporating the secondary element into the coating by pack codeposition, or (2) deposition of the modifying element prior to an aluminization process by electroplating, electrophoresis sputtering, chemical vapor deposition, or pack cementation [27].

Platinum, a relatively inert metal, is added to improve the hot corrosion resistance of an aluminide coating. This effect is strongly influenced by processing procedures for the coatings [29]. Platinum has shown significant benefits on the oxidation resistance of both low activity and high activity PtAl coatings [30]. Platinum promotes the formation of thinner and purer Al_2O_3 scales during the early stages, lowers the rate of β -NiAl degradation, and delays the onset of scale spallation. Platinum-modified aluminide coatings develop a spectrum of two-zone and three zone structures of standard aluminides depending on processing and the heat treatments involved [31]. In PtAl systems, platinum diffusional processes behave in a similar manner as does nickel in NiAl where stoichiometry plays a strong role [25]. Pt is relatively immobile in the Al-rich NiAl phase and highly mobile in the Ni-rich NiAl phase. Platinum is believed to promote Al_2O_3 -rich scale formation on $\gamma + \gamma'$ alloys in part because platinum addition appears to decrease oxygen permeability into the alloy [32].

Overlay MCrAlY coatings are applied by either electron beam physical vapor deposition (EB-PVD) or by thermal or plasma spraying where M is Fe, Co, Ni, or a combination of these elements. Typically these coatings initially contain cobalt or nickel, with 15-wt.%Cr, 12-wt.% Al, and 0.1-0.9-wt.%Y. To improve its resistance to Type II hot corrosion, the cobalt was partially replaced with nickel, the aluminum content was reduced somewhat, and the chromium content was increased from 15-20-wt.% to almost 32-wt.%. Hafnium is used as a replacement for yttrium in some MCrAlX coatings, where X (Y or Hf) promotes coating adhesion and oxidation resistance under thermal cycling conditions. In recent years, MCrAlY coatings have been air plasma sprayed (APS) as a cost-savings procedure and for reportedly better control of chemical composition. There are various procedures and methods by which plasma spraying may be done, many of which are proprietary or patent-protected. The principal oxide in the outer portion of a MCrAlY overlay coating is Al_2O_3 . Yttrium is more prevalent in the outer scale and promotes alumina formation for improved oxidation resistance and better scale adherence. Hafnium also promotes oxidation resistance and like yttrium, prevents sulfur from segregating to the coating/substrate interface, thus providing one mechanism of improving the overlay coating adhesion.

Ni, Co, or both and chromium are found in the inner half of the coating nearer to the coating/substrate interface. Increases in chromium content improve both the hot corrosion resistance and the oxidation resistance of the overlay coating, but tend to make the coating less ductile.

Marine gas turbine engines, until recently with the introduction of the MT30 and LM2500+ engines, have not required the use of thermal barrier coatings. Thermal barrier coatings (TBCs) usually consist of a porous layer of zirconia, ZrO_2 that is stabilized in the cubic crystalline structure by approximately 8 wt% yttria, Y_2O_3 . The yttria-stabilized zirconia (YSZ) is applied using either plasma spraying or by EB-PVD over a bond coat which is usually MCrAlY (where M is Co and/or Ni) or a diffusion aluminide. The bond layer is typically 75-125 μm and the TBC is 125-375 μm thick. Application of the TBC system to hot section components in a gas turbine decreases the superalloy substrate surface temperature by about 150 $^\circ\text{C}$. TBCs also smooth out hot spots thus reducing thermal fatigue stresses. A thermally grown oxide (TGO) layer is formed during coating application and tends to grow thicker upon high-temperature exposure of the porous TBC.

EB-PVD-applied TBCs tend to produce a columnar structure with fine ribbon-like voids and porosity within the columns aligned normal to the plane of the coating and superior compliance to residual stresses. Plasma sprayed TBCs has disk-like voids aligned parallel to the coating plane and promoting superior insulating efficiency.

There are a number of degradation modes which can limit the life of a TBC [33] as a result of oxidation due to the possible porosity network in the TBC. By understanding the specific thermomechanical failure modes, TBCs can be designed for greater reliability and durability [34]. EB-PVD TBCs tend to spall at the TGO/bond coat interface or in the alumina layer [35]. It has been observed that intermittent water vapor has degraded the adherence of alumina to the bond coat under a TBC layer more severely than alumina formed on the same bond coat in the absence of a TBC [33]. Salt deposition on TBCs of marine gas turbine engines tends to shorten the overall coating life by permeating into cracks and voids of the thermal barrier coating in the liquid or gaseous state and spalling when accumulated salts condense and solidify.

SUPERALLOY SUBSTRATES

Nickel-base superalloys have been an extraordinary class of materials that have been crucial to the continued development of high performance turbine engines. These superalloys have been the primary material for load-bearing structures because they have the highest homologous temperature of any common alloy system ($T_m = 0.9$, or 90% of their melting point). The widespread use of nickel-based superalloys in turbine engines coupled with the fact that the thermodynamic efficiency of turbine engines is increased with increasing turbine inlet temperatures has, in part, provided the motivation for increasing the maximum-use temperature of superalloys. Environment regulations restricting greenhouse gases such as CO₂, reducing specific fuel consumption, increasing power, or increasing the overall thermodynamic efficiency of the Brayton cycle has triggered the development of more efficient engines [30] requiring more advanced materials.

During the past 30 years turbine airfoil temperature capability has increased on average by about 4°F per year. Figure 1 shows these advances. This has been made possible by: (1) advanced processing to improve alloy cleanliness and/or producing directionally solidified or single crystal alloys that provide higher strength capabilities, (2) alloy development resulting in higher-use-temperature materials primarily through the additions of refractory elements such as Re, Ru, W, Ta, and Mo while reducing Cr, (3) use of thermal barrier coatings, and (4) innovative, effective cooling schemes. New generations of superalloys provide greater strength the Ni-alloys with higher refractory content are susceptible to long-term microstructural instabilities that form topologically closed packed (TCP) precipitates [36]. The lack of chromium in alloys intended for aircraft applications can further accelerate formation of TCP phases and development of alloy sulfidation [37].

Some progress has been made to identify a synergistic relationship between Cr, Mo, Re, and W during solidification of Ni-base superalloys [38]. However, an improved understanding of the subtle elemental interactions with these complex Ni-base alloys must be developed as a function of chemistry, processing, and service conditions in order to provide predictable resistance to high temperature deformation and environmental exposures.

DEVELOPING FUTURE ENGINE NEEDS FOR THE FLEET

All marine gas turbines currently in the Surface Fleet were derived (marinized) from aircraft engines. For the U.S. Navy, only GE and Rolls Royce are currently manufacturers of marine gas turbine engines for propulsion and auxiliary power. The 501-K17 and 501-K34 were derived from Rolls Royce T56 Series III and T56-427 aero engines [39]. The GE LM2500 was derived from CF6 and CF39 aero engines [39]. Using aero-derived engines for developing marine gas turbines is due in part to minimize costs for engine development. There are only a few marine gas turbine engines needed each year and the availability is, in part, leveraged by the market for industrial engines.

During the inception of the SPRUANCE Class program in the 1970's, Navy headquarters (Naval Sea Systems Command, NAVSEA) made a decision to utilize the LM2500 gas turbine engine at a part

power rating for its application (all gas turbines in the U.S. Navy were certified at a part power rating). That decision was made based upon a number of factors including lack of marine experience with gas turbine engines, interest in minimizing life cycle costs and OEM recommendations. The result of the decision to de-rate these engines has been a realized Mean Time Between Removal (MTBR) of 10 times its original projection and a Mean Time Between Failure (MTBF) of 5 times the original projection [40]. Hot section components typically have operated 21,000-27,000 hours MTBR from de-rated operations [39, 40].

However, in the last few years, some ships have pushed the operating envelope with disturbing results. As an example of pushing gas turbine power rating and the resultant engine life, during the 1991 Gulf War, the United States Military determined that a heavy lift capability was needed to move military equipment quickly to and from hostile locations. The American Bureau of Shipping (ABS) was used for the first time by the Navy to classify and certify these gas turbine powered ships using engine OEM proprietary design information to assess the ship's capability for safe operation. ABS certified a continuous power rating for the LM2500 engines used aboard T-AKR class ships at 32,000hp/engine [40]. The high power operations were in part required to achieve rated vessel speeds between ports. It is important to note, that while these high temperature/high power operations were beyond Navy surface combatants limits (T5.4 Alarm 1575°F), they were well within the engine controllers alarm setpoints for these ships. In effect, the operating crew did not exceed any control system parameters to achieve rated ship speed and shaft horsepower [40].

However, these ABS power-rated ships, after operating for only 7,800 hours, were observed by an OEM representative, performing a routine borescope inspection for ABS class certification, to have numerous HPT Stage 2 nozzles, which had large sections of airfoils missing or compromised beyond technical manual service limits [40]. It was confirmed via metallurgical examination that nickel-based superalloy vanes had experienced temperatures up to 1900°F (1038°C) for portions of its operating life. These findings confirmed that prolonged exposure to excessive operating temperatures caused component failures in service, resulting in oxidative overheating. These findings are consistent with ship-provided operating profiles which confirmed routinely exceeding the Type I and II operating regimes and in essence exceeding the material properties of the hot section components [40].

The Navy plans to utilize its first LM2500+ engine on LHD 8, an amphibious assault ship. This is the first application of this gas turbine engine on a non surface combatant and will represent the first LM2500+ engine in Navy inventory. The LM2500+ gas turbine engine, rated by ABS, operates somewhat differently than a base LM2500 in Navy applications in that its high power operations are T3-limited (compressor exit temperature). Based upon the 500 hour testing completed for rating purposes, the correlating T4.8 (T5.4) firing temperature is 1632°F (889°C). This operating point exceeds standard Navy temperature limits by more than 50°F (28°C). It is unknown how often the LHD 8 will perform at the maximum power scenario. Operations at high temperatures, greater than 954°C (1750°F), will result in oxidation as the primary deterioration process [40].

The power requirements of engines have been steadily increasing over the last 30 years as shown in Figure 2. Although the Navy believes its condition-based approach has proven cost effective for its legacy fleet, it is clear that future gas turbine designs may benefit from alternate maintenance philosophies due primarily to more aggressive operating profiles, which, in most cases, will push the operational envelope of the engine to its extreme material limits and beyond [40]. Future marine gas turbines will be integrated with electric drive and will provide source of power and energy to drive future propulsion requirements, energy-intensive weapons like electromagnetic rail gun and pulsed power, along with employing survivability measures such as electric armor. The materials for ever increasing power requirements will need to be addressed.

U.S. NAVY FUELS NEEDS

The availability of petroleum-based fuels is declining and the cost of petroleum has soared to over \$100 per barrel. The demand for petroleum is causing a global shift towards considering the use of alternative fuels. The world's navies are attempting to meet a need to be able to operate worldwide in an economy where petroleum-based distillate fuels may come scarcer and are increasingly mixed with synthetic fuels derived from biomass and other feedstocks. Future synthetic fuels, such as biodiesel, may be derived from Fischer-Tropsch (F-T) processes or by various processes. It is essential that whatever synthetic fuel is utilized for the U.S. Navy does not impose an adverse impact to current Fleet engines.

The Fischer-Tropsch reaction converts a mixture of hydrogen and carbon monoxide – derived from coal, methane or biomass – to liquid fuels. The Fischer-Tropsch process was discovered by German scientists and used to make fuels during World War II. The Fischer-Tropsch process converts the feed gas into liquid organic compounds, carbon dioxide and water. The conversion takes place in the presence of a catalyst, usually iron or cobalt. The temperature, pressure and catalyst determine whether a light or heavy syncrude is produced. There has been continued interest of varying intensity in Fischer-Tropsch technology ever since. SASOL in South Africa has produced liquid fuels from coal for approximately 30 years.

The Department of Defense (DOD) has an interest in F-T fuels because they will lessen dependence on foreign oil, reduce the number of different fuels required, and reduce environmental impacts because they burn cleaner than other liquid fuels. The U.S. military is the world's largest buyer of fuel, consuming 8 billion gallons per year. The DOD and DOE have partnered with Syntroleum Corporation to produce raw liquid F-T fuels from natural gas, which are further refined to create jet and diesel fuels [41]. These highly-isomerized fuels have branched and straight chain alkanes and few alkenes, but no aromatics or oxygenates. Syntroleum's diesel fuels have been engine tested and produce very little particulates or pollutants. Their jet fuel, mixed 50:50 with conventional petroleum-derived fuel, has recently successfully been tested by the Air Force in a flight of a B-52 jet with half of its eight engines fueled by the mixture [42].

The objectives of this DOE/DOD effort [41] are: (1) to overcome obstacles that prevent fully synthetic F-T jet fuel from being usable in jet engines and diesel land vehicles and to contribute to the development for a fuel specification for such use, (2) to better understand the relationship between the composition and properties of reformable liquid fuels, (3) to identify additives appropriate for F-T fuels that improve their compatibility with fuel system components, (4) to study accelerated fuel oxidation and thermal stability of F-T fuels as they are impacted by the use of additives, and (5) to develop and deploy advanced analytical and experimental methods to characterize the cracking and thermal oxidation products of F-T jet fuel.

However, the Fischer-Tropsch process may exacerbate the production of gases attributed to the increase of global warming. The U.S. Congress passed legislation to prevent federal agencies from procuring synthetic fuels which have a larger carbon footprint larger than petroleum-based fuels [43].

No Federal agency shall enter into a contract for procurement of an alternative or synthetic fuel, including a fuel produced from nonconventional petroleum sources, for any mobility-related use, other than for research or testing, unless the contract specifies that the lifecycle greenhouse gas emissions associated with the production and combustion of the fuel supplied under the contract must, on an ongoing basis, be less than or equal to such emissions from the equivalent conventional fuel produced from conventional petroleum sources.

Biofuels are being introduced into the supply system and may affect engine operations. Biodiesel is a Fatty Acid Methyl Ester (FAME) derived from its feedstock (a triglyceride) through the

transesterification process. Biodiesel is defined by the World Customs Organization (WCO) as “a mixture of mono-alkyl esters of long-chain [C16-18] fatty acids derived from vegetable oils or animal fats, which is a domestic renewable fuel for diesel engines and which meets the U.S. specifications of ASTM D 6751 [44]. However, biodiesel composition varies greatly as a function of geography and correspondingly different biomass sources. Biomass can be fruit and seeds from a wide range of plants. The primary biodiesel feedstocks are rape (canola), soy, and palm oil. The first two are preferred due to their better low temperature performance with a cloud point that is below 0°C. The range and standard composition of biodiesel throughout the world is very broad as the creation of biodiesel is largely uncoordinated and unregulated. Biodiesel can actually be made from everything between chocolate and chip pan fat through to a refined canola (rapeseed oil). It is the rapeseed oil feedstock, which when converted to Rape Methyl Ester (RME) oil, is considered to be one of the best sources of biodiesel from a European perspective and it is one of the feedstocks most likely to become an international biodiesel standard [45].

The reliable storage and use of fuels onboard warships is a key element in its ability to operate worldwide. There is much co-operation and sharing of information on naval fuels for this reason and the standards to be adopted has been widely researched [46]. NATO F-76, the current recommended fuel for shipboard operations, has a historical storage life of 3 years before degradation. When it occurs, three distinct mechanisms have been suggested for fuel destabilization: (1) biological contamination; (2) chemical destabilization of the fuel itself; and (3) potential for incompatibility when new fuel is mixed with remaining fuel in tanks.

As mentioned before, Navy Purchase Description (NPD) MGO fuel is subject to standard commercial practice quality control rather than the extensive handling and storage requirements specified for MIL-SPEC fuels. Table 1 shows the relative compositions of the two fuel specifications. There have been several reports that use of MGO has increased hot corrosion of gas turbine components and that it has limited physical stability. A conservative estimate of six weeks has been established for the complete use of MGO aboard USCG ships; this use limitation is viewed as operationally unrealistic. Any residual MGO in storage tanks can act as a catalyst to degrade newly introduced fuel.

In 1996, the US Navy surveyed and evaluated commercial MGO fuel samples from 42 suppliers from around the world. Thirty-four MGO fuel samples had at least one property that failed NATO F-76 specifications. One fuel sample showed excessive levels of trace elements such as calcium, sodium plus potassium, lead, and vanadium. Copper affects fuel stability, lead forms low-temperature eutectics, sodium and potassium contribute to increased hot corrosion, and vanadium at sub-ppm (~ 0.3 ppm) levels accelerates hot corrosion. Calcium acts as surface glue that enhances corrosion activity.

The introduction of alternative fuels will reduce dependency of petroleum-based fuels for the U.S. Navy and the rest of DOD. However, there are limited specifications for these synthetic fuels. Both Fischer-Tropsch and bio-derived fuels have almost zero sulfur content. Water content is considered important because sodium impurities from sea water can cause corrosion of combustors in a relatively short time if not suitably managed. Unfortunately, biofuel is known for being highly hygroscopic although it is not known to be miscible with water. The water content can be as high as 1,200 ppm in biodiesel, although the standards specify a 500 ppm limit.

All diesel and gas turbine engines have had some reliance on diesel fuel as a lubricant. The lubricity of petroleum-based fuel, and correspondingly the concentration of aromatics in the fuel, has been an indication of the amount of wear or scarring that occurs between two metal parts covered with the fuel as they come in contact with each other. Low aromatic, low lubricity fuel may cause high wear. The lack of aromatics in Fischer-Tropsch fuels also reduces the degree of

swelling of gaskets of some organic compositions and lacks the lubricity of petroleum-based MIL-SPEC fuels.

The introduction of ultra-low sulfur diesel (ULSD) (< 15 ppm sulfur) has introduced new problems. Gelling of ULSD in cold temperatures has occurred even when anti-gelling additives have been used [47]. It is believed that ULSD will likely have water issues, which could mean increased microbial growth. The actual composition of ULSD is a little different, depending on the crude oil source and how it was processed at the refinery to achieve the ultra-low sulfur fuel. While water has always been a common component of diesel fuel, it acts differently in ULSD, in ways that can cause greater problems in the transportation engines and increased free water in storage tanks [47]. In ULSD, sulfur, a natural biocide, is no longer present in enough quantity to perform that function of killing microbes.

The U.S. Navy Fuels and Lubricants Integrated Product Team currently does not recommend the use of biofuels for tactical vehicles (ship or aircraft) because biofuels currently increase operational costs, degrade quickly, and lack the storage stability of petroleum-based fuels [48]. In some areas of the world, biodiesel content has trickled into the Navy's supply system. The Navy's practice of using seawater to compensate ship fuel tanks needs to be explored to determine the effects of this practice on the synthetic fuel stability, microbiological activity, Naval engine performance, and materials resistance to fuel-related degradation. Preliminary results show that 20 vol% biodiesel with commercial petroleum-based diesel and B100 biodiesel were 40 and 100 times, respectively, more susceptible to biogradation/biocontamination than petroleum-based diesel [49].

Environmental Compliance

The U.S. Navy has attempted to comply with international, national, and local environmental regulations. In October 2008, the International Maritime Organization (IMO), with the U.S. Navy as an active participant, adopted an aggressive program to control air emissions from oceangoing vessels (OGVs) [50]. Ships operating in areas with air quality problems, designated Emission Control Areas (ECAs) will be required to meet tighter emission limits. More than 40 ports in the U.S. are in metropolitan areas that currently do not meet EPA air quality standards. Beginning in 2015, OGVs operating in these affected areas will be required to use fuel with no more than 1,000 ppm sulfur, a 98% reduction from the global sulfur cap today. Beginning in January 2016, new ships operating in ECAs must also have advanced-technology engines that cut the nitrogen ozone-reducing oxides, NO_x by 80%. The new fuel standards will phase in over time, starting in July, 2010 when ECA fuel sulfur standards will be 10,000 ppm [50].

FUTURE RESEARCH DIRECTIONS

To achieve the long-term goal of developing new high temperature propulsion materials to meet the capability needs of the U.S. Navy, multi-disciplinary basic and applied research will be required. The life of ultra-high temperature materials in engines (shipboard or aircraft) is dependent on a complex combination of temperature-stress- environment- time variable fields. Materials in turbine engines from the Navy as well as Army and Air Force must withstand the dynamic effects of various environments (oxidization, corrosion, salt, thermal cycling, sand ingestion, foreign object impact), fuel combustion, intrinsic and extrinsic materials properties, and varying operational parameters.

The objectives of the basic research will be to explore high-temperature mechanisms from the atomic- and molecular-scale to macroscale level in order to create physics-based and thermo-mechanical-based models to establish the fundamental, scientific understanding of high-temperature materials and/or coatings under the influence of complex, interacting variables such as chemical activities, multi-element diffusion, kinetics, mechanics, and thermodynamic contributions in order to

survive up to 1500°C over a wide range of stress-environment-time variable fields. This may include molecular dynamics that explores the multiscale role of defects [point defects (vacancies, interstitials), linear (dislocations), and planar (grain boundaries, stacking faults, interfaces)] in initiating cracking and fracture. Research should include how to manipulate defect mobilities under a range of composition, mechanics, and environment to establish intra- and interfacial resistance to cracking and fracture.

The research will require an interdisciplinary research team that can couple materials science, interfacial and surface science, materials chemistry, corrosion and electrochemistry, fluid and solid mechanics, diffusion, biology and microbiology, multi-scale thermodynamic and kinetic modeling and simulation, and atomistic characterization to develop advanced materials systems. The materials systems that optimize microstructures, interfaces, and surfaces that will minimize defect mobility and/or impurities; increase chemical, environmental, and thermal stability; retain strength and creep resistance at very high temperatures for improved capabilities and predictive multi-variable models for operational life. The research will integrate the fundamental understanding of single or coupled degradation mechanisms of these materials/materials systems with ultra-efficient cooling schemes.

Advanced Engines

The operational profile of current U.S. Navy surface combatants varies depending upon the ship's mission; more than half of all operations are at less than 50% power [39]. Many future ships will be designed to operate in higher horsepower states compared to traditional U.S. Navy standards. Ultimate component and engine life will be dependent on the actual operating profile.

Future advanced turbine engines will employ various concepts to improve power, increase efficiency and reduce overall fuel consumption. The U.S. Air Force is funding development of The Adaptive Versatile Engine Technology (ADVENT) program which aims “to develop and demonstrate inlet, engine, exhaust nozzle, and integrated thermal management technologies that enable optimized propulsion system performance over a broad range of altitude and flight velocities. This new engine design, based on the Brayton cycle, will generate high thrust when needed, and optimize fuel efficiency when cruising or loitering, in order to combine the best characteristics of high-performance and fuel-efficient jet engines. Marinization of this engine (scheduled for AF demonstration in 2012) might be able to deliver engine power to match real time ship power demands. This would potentially maintain running the engine in its most efficient performance range, thus allowing improvement in specific fuel consumption, increasing ship range, and simplify the use of multiple engines sizes for propulsion and auxiliary power.

Other engine technologies such as HEETE (highly efficient, embedded turbine engine) may utilize increased pressures. Pulse detonation engine or more advance engines using constant volume (Humphries) thermodynamic cycles may increase the energy densities, engine efficiencies, and reduce specific fuel consumption for aircraft engines, which can be, if economics warrant, be marinized to develop future advanced marine gas turbines.

Materials - substrates

If development of advanced turbine engines continues to require higher temperatures and/or pressures, it will require the improvement of existing materials and the creation of new materials to meet the challenges of increased temperatures and/or pressures operating in potentially more aggressive, hostile environments while meeting still meeting Fleet MBTRs and MTBFs. The successful application of high temperature structural materials for marine gas turbines is reflected in a variety of thermomechanical and thermochemical properties: strength, ductility, toughness, phase stability, fatigue resistance, creep resistance, oxidation resistance, corrosion resistance and resistance

to other environmental stimuli. Since history has shown that a single phase is unlikely to satisfy all of these properties, multiphase material designs are desirable.

As marine gas turbine engines move above 950°C, oxidation becomes the primary mode of environmental degradation at full power. However, these materials will also need to be resistance to hot corrosion when engines are at less than full power when prevailing temperatures are 650°C to 950°C. The cycling between oxidation and hot corrosion regimes will place added needs for resistance for multi-mode environmental attack. Recent experimental work indicates that a one hour exposure to Type II corrosion environment significantly degraded the oxidation resistance of uncoated superalloys [51]. Remarks in a 2003 Workshop on land- and sea-base turbines stated that there was no model linking hot corrosion resistance with other important coating properties such as thermal conductivity or thermal expansion. In particular, there is a lack of ‘interdisciplinary’, physics-based models linking mechanical and environmental interactions [52].

There is a need to develop, validate, or modify physical scale, mechanistic, or computational models linking materials to mechanical, thermal, and/or corrosion to achieve predictive capability. These models may also provide a basis for limited extrapolation. High-fidelity models need to include the multitude of factors that influence the thermodynamics and the kinetics of corrosion for a range of materials. A plethora of molten and gaseous high-temperature degradation processes are affected by a different mix of primary, secondary, and non-participatory factors which, to varying degrees, influence the corrosion and the thermomechanical performance of materials.

As mentioned earlier nickel-base superalloys have been an extraordinary class of materials that have been crucial to the continued development of high performance turbine engines. These superalloys have been the primary material for load-bearing structures because they have the highest homologous temperature of any common alloy system ($T_m = 0.9$, or 90% of their melting point). The widespread use of nickel-based superalloys in turbine engines coupled with the fact that the thermodynamic efficiency of turbine engines is increased with increasing turbine inlet temperatures has, in part, provided the motivation for increasing the maximum-use temperature of superalloys. Environment regulations restricting greenhouse gases such as CO₂, reducing specific fuel consumption, increasing power, or increasing the overall thermodynamic efficiency of the Brayton cycle has triggered the development of more efficient engines [36] requiring more advanced materials.

As temperatures continue to increase, other materials for possible insertion into marine gas turbine engines need to be considered. Elevated temperatures limit the number of possible materials classes: ceramics, intermetallic alloys and refractory metals such as Nb, Mo, W, and Ta. As single components, ceramics and intermetallic phases are known to suffer from embrittlement at low temperatures. Refractory metals such as Nb and Mo have sufficient ductility but suffer from oxidation.

Mo-based alloys and ceramic matrix composites are two materials classes that are being pursued for aircraft engine applications. The Mo-Si-B alloy system has high temperature stability (melting temperature, T_m , is above 2000°C) and attractive materials properties for different combinations of equilibrated phases. The oxidation behavior of the Mo-Si-B system has been documented [53, 54]. Three phase alloys comprised of Mo (solid solution (ss)), T2 (Mo₅SiB₂) and Mo₃Si offer favorable combinations of high temperature mechanical properties and oxidation resistance due to the formation of an adherent borosilicate layer during high temperature oxidation [55]. Similarly, a combination of mostly the Mo₅Si₃ (T1) phase with T2 and MoB phases shows an excellent oxidation resistance comparable to that of MoSi₂ [56] due to the formation of a borosilicate layer which functions as an effective oxygen diffusion barrier also.

A number of alloy compositions have been identified that exhibit good oxidation resistance at high temperatures due to formation of a borosilicate glass on the surface of the alloys that inhibits oxidation.

Above 800°C, the oxidation of the Mo–Si–B alloys can be described by two stages. In the first stage the molybdenum present on the surface reacts with oxygen to form the volatile MoO₃ compound. This is called the transient oxidation stage. The silicon and boron are oxidized as well and the borosilicate layer starts to form. The second stage appears when the sample is completely covered by the protective borosilicate. Then, the mass variation and the alloy rate of recession are considerably reduced. The response of Mo–Si–B alloys to oxidation is sensitive to their composition. The B to Si ratio controls the constitution of the in situ SiO₂–B₂O₃ passive layer that forms upon oxidation. Increasing the B to Si ratio decreases the viscosity of the glass and allows it to cover the surface of the sample faster and reach the second stage of oxidation the steady state sooner [57]. On the other hand, it also increases the oxygen diffusivity through the glass and lowers the high temperature oxidation performance. At low (650–750°C) temperatures, the formation of a protective borosilicate layer is slow compared to the loss of Mo by the formation and volatilization of MoO₃ and leads to peeling.

Ceramic-Matrix-Composites (CMCs) have been developed to overcome the intrinsic brittleness and lack of reliability of monolithic ceramics. A given ceramic matrix can be reinforced with either discontinuous reinforcements, such as particles, whiskers or chopped fibers, or with continuous fibers. In the first case, the enhancement of the mechanical properties, in terms of failure strength and toughness, is relatively limited but it can be significant enough for specific applications. Discontinuous whisker reinforcements are by far the most attractive in terms of mechanical properties.

There is a wide spectrum of CMCs depending on the chemical composition of the matrix and reinforcement chosen. Non-oxide CMCs are by far those which have been the most studied. The best performing fibers, in terms of stiffness, failure strength, refractoriness and density are non-oxide fibers, i.e. carbon and silicon carbide fibers. In order to avoid compatibility problems, which are crucial at high temperatures, non-oxide fibers are preferably embedded in non-oxide matrices. Hence, the first non-oxide CMC has been carbon/ carbon (C/C) composite. C/SiC and SiC/SiC composites were developed in order to increase the oxidation resistance of the materials and hence their lifetimes in oxidizing atmospheres. Silicon nitride has also been used as matrix although it is less stable at high temperatures than silicon carbide.

Oxide-CMCs, from a thermodynamic standpoint, should be stable for long-term applications in oxidizing atmospheres. Unfortunately, oxide fibers, although they are refractory, tend to undergo grain growth at high temperatures, (which results in fiber strength degradation) and exhibit poor creep resistance. Further, they display much higher densities than carbon fibers. Attempts have been made to improve the high temperature properties of oxide fibers with limited success. Despite these disadvantages, Al₂O₃/Al₂O₃ and derived CMCs have been, and are still, extensively studied.

To further improve the capability of CMCs and create new materials an understanding of the micromechanics damage involving matrix cracking, interface debonding, delamination and/or fiber fracture, damage accumulation and failure under stress gradients, failure mechanisms associated with fiber architecture inhomogeneities will need to be established [58]. Models that include bridging and clumping of fibers and fiber coatings, component design for stress state optimization accounting for gradients, transients, attachments, & interactions, complex interactions, such as failure from thermal stress, thermal cycling and gradients, multiaxial stress states, vibration, and environmental effects, and environmentally assisted subcritical crack growth will help launch this understanding. Many synergistic interactions such as the relationship between matrix microcracking and fiber-matrix interphase oxidation or interphase and matrix oxidation from environmental coatings failure and surface recession have been largely unexplored. Materials failures from active or passive oxidation of SiC fibers need to be understood.

Environmental effects and life prediction of on materials have tended to be one-dimensional, exploring the passivity and breakdown resistance of materials in environments known to cause

oxidation, hot corrosion, sulfidation, chloridation, etc. However, in actual service environments, materials may be exposed to mixed environments over time. Recent research revealed that high temperature coatings exposed to a hot corrosion environment for one hour significantly altered the oxidation resistance of the coatings for the next 1000 hours. The fundamental understanding for this behavior is yet unexplored but needed to establish life prediction models [58].

Coatings

For coatings (i.e. diffusion, overlay, thermal- and environmental barrier) to successfully protect advanced materials there needs to be a fundamental understanding of the thermomechanical and thermochemistry factors that lead to long-term coating stability when exposed to oxidation and more complex corrodants that is likely to occur in advanced marine gas turbine engines [59].

Nickel-base superalloys, Mo-Si-B alloys, CMCs, or other ultra-high or high temperature material substrates need to be protected from environmental degradation. High temperature coatings generally form alumina, chromia, or silica protective scales. A protective oxide depends on many variables, not all of which have been identified or understood [60].

It is generally accepted that (environmental barrier coatings) EBCs are employed to protect silicon-based ceramic components from high temperature environmental attack. With increasingly higher demands for high engine operating temperatures in the future, environmental barrier coatings (EBCs) need to be designed to offer both thermal and environmental protection of engine components.

Si-based ceramics have excellent oxidation resistance due to the formation of SiO₂ layer at the surface when exposed to high temperature oxidative environments. However, SiO₂ scales react in complex combustion environments containing corrosive oxides Na₂O, V₂O₅, SO₂, and/or SO₃, or water vapor. These complex, corrosive gases react with protective silica scales to form non-protective low melting temperature silicates. Water vapor volatilizes the silica in protective coatings to gaseous Si-O-H species, thus degrading the coating and eventually exposing the bare ceramic surface.

Since the melting temperature of silicon is 2550°F (~1400°C), any coating and CMC that are needed to perform in the (1480-1650°C (2700-3000°F) range will need to eliminate silicon from the system. The silicon bond coat serves two equally important functions in the current state-of-the art EBCs – enhancement of adhesion to the CMC and oxidation protection of the substrate (by gettering oxygen).

EBCs must meet several requirements: (1) the coating surface must be environmentally durable to aggressive species; (2) the coating needs to act as an effective diffusion barrier; (3) it must be mechanically tough, free of cracks, avoid deleterious phase changes, and have a coefficient of thermal expansion that is closely matched with the substrate; and (4) the coating should have good chemical compatibility with the substrate to promote good adhesion [61].

Silica-forming coatings are able to provide a good oxidation protection of the Mo-Si-B alloys in dry air but will be reactive to water vapor at temperatures above 1000°C [62]. Applying aluminum pack cementation on Mo-Si-B alloys provides a coating rich in the Mo₃Al₈ phase [63]. When subjected to oxidation, at temperatures varying between 700 and 1372°C, the Mo₃Al₈ phase reacts with the oxygen to form alumina on the surface of the coated alloy and protects it from further oxidation, even at low temperatures [63]. The oxidation under thermal cycling conditions reveals that the thermal expansion mismatch between the coating and the substrate is high and leads to the formation of cracks during cycling to 1300°C. However, the results also have shown that the coating has a very good healing capacity due to the rapid formation of alumina in the cracks [57].

Improvement of TBC system components will augment the service life of thermal barrier coatings. TBC failure often occurs at or near the TGO-topcoat interface. Therefore, the TGO is critical to the

development of durable and reliable TBCs. The TGO growth needs to be slow, planar, be adherent to the bond coat and the top coat, and avoid interdiffusion from the bond coat. The performance of the TGO is linked to the structure and composition of the bond coat. The bond coat must have excellent oxidation and/or corrosion resistance, intrinsic resistance to the development of surface undulations, thermal and physical compatibility with both the alloy substrate and the ceramic topcoat. The choice of a bond coat has traditionally been either a MCrAlY overlay (where M=Ni, Co, or both) or a beta platinum-modified nickel aluminide (β -(Ni,Pt)Al). However, using first principles and integrating thermodynamics and kinetics, a new family of Pt-modified γ -Ni+ γ' -Ni₃Al compositions have been discovered that possess “ideal” bond coat characteristics [64-71]. These new bond coats are phase-compatible with current and next-generation superalloy substrates, which should help minimize both coating/substrate interdiffusion and the mismatches of coefficients of thermal expansion. The Pt decreases Al activity and partitions solely to Ni sites and decreases oxygen permeability in γ and γ' . These select Ni-Al-Al alloy compositions are also resistant to martensitic transformation. The addition of Hf to certain Ni-Al-Pt compositions has decreased oxidation to by an order of magnitude [69-71].

Coating performance and life prediction is complicated by: (1) application process; (2) processing variables; coating structure and composition; and (4) substrate structure and composition. Different substrates may cause vastly different coating performance of the same composition. Different coating application processes may also greatly alter the performance of the same coating and of the substrate interactions with identical coatings [59].

A better understanding of physics and fluid dynamics of all application and processing steps for the various coating systems is needed. Potentially improved coating systems are application-limited by the scope of our present understanding and control of processing [63]. Coating compositions must be tailored for the chosen deposition process (EB-PVD, plasma spray, electrodeposition, electrophoresis, etc.) and the chosen substrate. The basis for potentially detrimental substrate interactions with coatings from interdiffusion must be thoroughly understood and considered in the early phases of substrate/coating development [72].

The performance of a high-temperature coating is dependent on the substrate and on the coating application process [72]. Identical coatings applied on different substrates do not behave in the same way. Identical substrates may not behave equally because casting parameters and structural segregation and processing may differ from one sample lot to another [72]. Coatings cannot be successfully developed without considering substrate effects and the variables in coating fabrication processes. Coatings applied by different techniques do not perform identically in terms of performance/lifetime because the process and heat treatment variables may vary in different lots or from different coating suppliers [72].

There also needs to be an increased understanding of the coatings manufacturing methods, coating structure, corrosion mechanisms, and coating failure mechanisms [73]. Good quality control during coatings application avoids process artifacts, coating defects, or contamination that may affect accurate evaluation of failure mechanisms by providing easy pathways for the environment to penetrate the coating. Quality control also ensures that substrate cleanliness is maintained during high temperature coating application and that the coating integrity (coating adhesion, porosity, etc), and surface finish that will reflect the true coating resistance to low temperature and high temperature hot corrosion [74]. The utilization of thermodynamically-based modeling and development of multi-component phase diagrams will help predict possible harmful phases in the development of new high-temperature alloys and coatings.

Interfacial Phenomena

Substrates and coatings for high temperature service are dynamic with time. The performance of alloys and coatings is dependent largely on temperature, stress, environment, and time. The

fundamental importance of surfaces, interfaces, grain boundaries, coating structures and associated structural defects, transport properties, and enrichment-segregation phenomena, is essential towards understanding substrate and coating degradation, and various corrosion pathways and mechanisms [75]. Phase transformations and surface reactions of a coating attacked by hot corrosion are basically the same as those that take place during oxidation, except that the overall rates during hot corrosion are much faster [76].

During service, coatings degrade at two fronts: the coating/gas-path interface and the coating/substrate interface. Deterioration at the coating/gas path interface is the result of interaction of the coating materials with the prevailing environment; a major contributor to coating degradation in marine gas turbine engines is hot corrosion. However, on the second front at the coating/substrate interface, interdiffusion contributes to coating degradation as a function of exposure time which is often less noticed, but is vitally important to the service life of high temperature coatings.

Coatings and superalloy substrates generally have widely diverse compositions due to the functional requirements of balancing mechanical properties with oxidation/corrosion resistance. Under such conditions, solid-state diffusion at the coating/substrate interface occurs. This interdiffusion causes compositional changes on both sides of this interface as a function of time and temperature; this can compromise the substrate properties and/or deplete the coating of critical species. Interdiffusion between the coating and the substrate [77] can modify the oxidation and corrosion resistance of the coating and the mechanical properties of the coating-substrate system. The presence of sulfide species in the coating may also lead to diffusion via grain boundaries or other relatively easy diffusion pathways into the substrate and/or into the coating. This may alter the long-term performance of a coating/alloy system in a hot corrosion environment in a way that would not occur in an oxidation environment [37].

POSSIBLE NEW CORROSION AND DEGRADATION MECHANISMS

In Naval aircraft over certain geographic areas, the ingestion of dust or sand in aircraft engines. Hotter engine temperatures have caused deposition of molten calcium-magnesium aluminosilicate (CMAS) to form on thermal barrier coatings, which has had the potential to significantly reduce the service life of TBCs [78]. At lower temperatures these solid contaminants can cause localized impact and erosion. At higher temperatures the siliceous debris adheres to the TBC surface and forms glassy melts. CMAS dissolves the metastable t' phase and reprecipitates with a structure and composition dependent on the local chemistry [6]. A large volume of CMAS causes reprecipitated YSZ to be sufficiently depleted of yttria that the zirconia transforms to the monoclinic phase. Molten CMAS penetrates through the TBC and causes thermomechanical spallation from the loss of strain compliance of the coating in the thermal gradient and solidification of CMAS [5,6]. The ingestion of chlorides and sulfates from the intake air may lower the temperatures where molten CMAS attacks engine materials on ships relative to that observed in aircraft engines.

Alternative Fuels

The Office of Naval Research (ONR) has initiated a program to determine the impact of utilizing synthetic alternative fuels such as Fischer-Tropsch and biofuels on Naval propulsion and auxiliary engines and storage stability. The aim of one project is to allow for predictions about storage and use of biodiesel and mixtures of biofuels with petroleum-based fuels [79]. Changing from petroleum to a mixture of biodiesel and petroleum diesel may increase the risk of microbiologically influenced corrosion (MIC) of fuel tank metals. Bacteria and fungi contaminate hydrocarbon fuels and can cause MIC. The total microbial population is limited by the availability of water, nutrients and electron acceptors. The specific constituents of the microbial community are determined by the composition of the fuel. The experiments

characterized the microbial community in petroleum biodiesel mixtures and determined the potential for these communities to cause corrosion to uncoated carbon steel, aluminum alloys, and stainless steels. Corrosion morphology was characterized by environmental scanning electron microscopy. Chemical analysis of fuels before and after exposure and genetic identification of dominant microflora is ongoing.

The current progress is briefly summarized. The approximately 1 Volt difference in measured E_{corr} values across the different exposure conditions for AISI 1020 carbon steel clearly demonstrates the differences in material/fuel mixture interactions for the different fuels as shown in Figure 3. In regards to corrosion rates: 1) AISI 1020 carbon steel in ULSD had the highest corrosion rate in this experiment, 2) 304L exhibited passive behavior in all fuel/water mixtures [79]. Carbon steel was observed to actively corrode in mixtures of ULSD and water after four days exposure time as shown in Figure 3a. Exposures to mixtures containing additions of biodiesel (BD) did not actively corrode. Biodiesel has the highest propensity for biofouling while the highest corrosion rates were measured in ultra-low-sulfur diesel.

Microbial influenced corrosion or biocorrosion is typically associated with the development of surface biofilms. A biofilm is a microbial assemblage enclosed by a matrix of extracellular polymeric substance and innervated by a network of channels. It is the community metabolism of such biofilms on metal surfaces that ultimately results in the failure of colonized structures under the ambient environmental conditions.

The use of ULSD may increase the occurrence of biocorrosion by one of three mechanisms [80]. First, the removal of organosulfur molecules from fuels or fuel mixtures results in less inhibition of the bacteria responsible for biocorrosion. The lack of inhibition then allows these deleterious organisms to proliferate, form biofilms and catalyze corrosion when they would otherwise fail to do so. Londry and Suflita found that thiophenes, thiols, thiophenic acids and aromatic sulfides could inhibit a variety of metabolic processes in anaerobic cultures enriched from an oily sludge [81]. Second, the metabolic fate of the residual organic compounds that enter fuels as a result of the selective removal of sulfur in the oil refining process may affect the development of biocorrosion. This will vary considerably depending on the composition of the feedstock. Lastly, the manufacture of ULSD results in several consequences including the loss of lubricity in the resulting product. The poor lubricity of ULSD mandates the use of additives or blending with another fuel of sufficient lubricity to restore that property. Typically, low levels of biodiesel (2-20%) are used to restore lubricity to ULSD. Biodiesels are inherently more susceptible to microbial decay since the component methyl esters are usually hydrolyzed with relative ease.

Recent preliminary research results clearly implicate that biodiesel suffers from an enhanced rate of biodegradation when compared to current Navy diesel distillate fuel: a microbial inoculum, when incubated with ultra-low sulfur diesel+biodiesel (20% v/v) or 100% biodiesel revealed a 40-fold and 100-fold greater susceptibility to biodegradation, respectively. It is suspected that enhanced biocorrosion will also be observed with biodiesel and its blends due to formation of multi-species microbial communities and/or biofilms. Sophisticated strategies for sequential processing of complex organic matter to increasingly more simple products, with concomitant production of potentially corrosive agents (i.e. CO_2 , various organic acids, nitrite, hydrogen sulfide, mineral acids, and redox-active electron shuttles) is known to occur within these consortia. In addition, electron transfer between organisms and with the underlying substrates results not just from seawater components and microbial metabolites that are generated, but through direct transfer of electrons via microbial nanowires.

Shifts within microbial consortia in response to changing environmental conditions are agile, and reflect their natural adaptive capabilities, and ability to communicate at an intra- and intercellular level.

For example, changes in ambient biogeochemistry (Fe, S, O₂, species), pH, Eh, availability of electron donors/acceptors will elicit re-structuring of the microbial community, and along with this process, differing sets of microbial products with the potential to effect corrosion or de-stabilize biofuels will form.

The microbial metabolism of fuel components results in the production of key metabolites, the identification of which can help pinpoint the critical organic compounds that support the entire microbial community. In addition, identification of microbes, key enzymatic pathways and mechanisms involved in biodegradation or biotransformation of biodiesel and resultant biocorrosion processes need to be elucidated to understand the ramifications of utilizing biodiesel-based fuels for Navy tactical platforms. It is further expected that variations among feedstock sources of biodiesel (rapeseed, Jatropha, palm, marine algae, etc) , esterification method, by-product removal method and storage conditions introduce other potential factors that can influence biodegradation and the rate and extent of biocorrosion. It is necessary to explore a diversity of both biodiesel stocks as well as possible microbial inocula obtained from facilities where they are prepared, handled, stored, and utilized in depot and/or ship settings.

Research will need to explore molecular- and microbiological approaches to establish the key organisms, reactions and mechanisms involved in biocontamination and subsequent biocorrosion processes in biodiesel based fuels. The identification of specific microbes; metabolites; functional genes (e.g. alkylsuccinate and alkylsuccinate synthase genes); fuel compounds, contaminants or reactive moieties; intra- and intercellular links as a function of environment, biodiesel source and biogeochemical conditions is needed. It is expected that increased understanding of these interconnected reactants and processes will lead to the discovery of metabolic pathways that support the origins of biocontamination and biocorrosion. This scientific foundation will then enable the creation of stable biofuels from renewable resources via innovative microbial synthesis and biotechnology.

NEW CONCEPTS

The life of ultra-high temperature materials in gas turbine engine (shipboard or aircraft) applications is dependent on a complex combination of temperature-stress-environment- time variable fields. Research must take a new approach to establish a solid science base that will achieve the development of new materials and coatings that will enable more efficient engines and to develop the life prediction capabilities for materials exposed in these temperature-stress-environment-time continua.

There needs to be a systems approach that dissects, then later reconnects the critical drivers that influence the performance and life of materials and coatings at high and ultra-high (above 1500°C) temperatures. The system needs to include the substrate, the coating, the intrafacial features within materials, the interfacial factors occurring between materials, and localization factors such as surface condition or microstructural features that may play a life-determining role. The system may be broken down into sub-systems to help simplify and refine different materials-related aspects of overall system.

The goal is to create multi-variable physics and chemical-based models and tools to establish the fundamental science base for ultra-high temperature material systems that can survive above 1500°C over a wide range of stress-environment-time variable fields encountered in future shipboard and military aircraft engine operations. Time should be viewed as the dependent variable that varies as a function of independent variables of temperature, stress, and environment. For instance, the life of a ship engine material as a function of fixed temperature and stress may be strongly dependent on the aggressiveness of the environment. The research will require an interdisciplinary research team that can couple materials science, interfacial science, materials chemistry, corrosion and electrochemistry,

fluid and solid mechanics, diffusion, multi-scale thermodynamic and kinetic modeling and simulation, mathematics, and atomistic characterization to develop advanced materials systems. It is anticipated that the validation of these models will help determine the life of materials and coatings (such as MTBF) that can exist with a given field of temperature, environment, and time.

A materials system concept will optimize microstructures, interfaces, and surfaces that minimize defect mobility and/or impurities; increase chemical, environmental, and thermal stability; retain strength and creep resistance at very high temperatures for improved capabilities and follow predictive multi-variable models for operational life. The research will integrate the fundamental understanding of single or coupled degradation mechanisms of these materials/materials systems with or without ultra-efficient cooling schemes.

Research should establish a basic understanding of performance-limiting mechanisms and control strategies for ceramic composites, intermetallic alloys, and protective coatings operating in multiple environments; establish microchemistry, microstructural phase fields, and analytical formalisms accounts for grain size effects that will predict intermetallic alloy thermal, stress, and environmental stabilities; determine 3-dimensional, multi-scale effects of impurities, chemistries, and environments on fiber/matrix interfacial mobility, to maximize micro-mechanical interfacial strength, creep, and thermal stability for establishing optimal composite properties; establish atomistic models and utilize characterization tools to determine diffusion-barrier capability, interfacial interactions, optimal architectures, chemical compatibility between matrix and fiber; and the coefficient of thermal expansion match between a fiber and its matrix. There is also a need to establish processing science protocols that link coating performance to substrate specifics, decrease application costs, and control the composition and structures of the coating.

The laboratory research has no lasting value unless the scientific foundation and the physical, chemical, and the thermomechanical models are validated by actual field tests or highly coordinated simulations. Interactions among academic research, government laboratory, in-service engineer, and original equipment manufacturers are cultivated and encouraged.

CONCLUSIONS

High temperature applications demand materials that have a variety of properties such as high strength, toughness, creep resistance, fatigue resistance, as well as resistance to degradation by their interaction with the environment.

A multidisciplinary systems approach needs to resolve the critical drivers that influence the performance and life of materials and coatings at high and ultra-high temperatures (above 1500°C). The system needs to include the substrate, the coating, the intrafacial features within and interfacial drivers between materials, and localization factors such as surface condition or microstructural features that may play a life-determining role. The system may be broken down into sub-systems to refine different materials aspects of overall system.

Using the overall systems approach, the goal will be to create multi-scale, multi-variable physics and chemical-based models and tools to establish the fundamental science base for ultra-high temperature material systems that can survive above 1500°C over a wide range of stress-environment-time variable fields encountered in future shipboard and military aircraft engine operations. It is anticipated that the validation of these models will help determine the life of materials and coatings that can exist given temperature, environment, and time (MTBR).

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Table 1- MGO and NATO F-76 Fuel Specifications [18] and Nominal NATO F-76 Values

Property	Units	ASTM Method	MGO-CG1 Specifications		NATO F-76	
			Min	Max	Nominal ⁽¹⁾	Specifications
Viscosity@ 40°C	mm ² /s	D445	3.00	4.00	3.35	1.7-4.3
Demulsification	Minutes @ 25°C	D 1401	--	--		10
Carbon Residue on 10% bottoms	wt %	D 524	0.30	0.35	0.10	0.20 max
Sulfur	wt %	D 4294/D 129	0.97	1.03	0.2	0.5 max
Cloud Point	qC	D 2500	record	record	-10	-1 max
Pour Point	qC	D 97	record	record	-5	-6 max
Distillation90%Pt	qC	D86	310	330	319	357max
Color	--	D 1500	record	record	<1.0	3 max
Flash Point	qC	D 93	60.0	--	93	60 min
Particulates	mg/l	D 6217	--	10	5	10 max
Hydrogen Content	wt %	D 4808	--	--		12.5 min.
Density @ 15.6 qC	kg/m ³	D 1298	836	876	840	876 max
Ash	wt%	D482	--	0.01	<0.001	0.005 max
Water & Sediment	vol %	D 2709	--	0.05	<0.005	
Water Content	ppm	D 1744	record	record	190	
Aniline Point	qC	D 611	--	--		60 min
Acid Number	mg KOH/g	D 974, D 664	--	--		0.30 max
Al	ppm	⁽²⁾ note 2	--	<0.1	<0.1	
Ca	ppm	⁽²⁾	--	<0.1	<0.1	1.0 max
Cu	ppm	⁽²⁾	--	<0.3	0.23	
Fe	ppm	⁽²⁾	--	<0.1	<0.1	
Pb	ppm	⁽²⁾	--	<0.1	<0.1	0.5 max
Ni	ppm	⁽²⁾	--	<0.1	<0.1	
Si	ppm	⁽²⁾	--	<0.1	<0.1	
K	ppm	⁽²⁾	--	<0.1	<0.1	
Na	ppm	⁽²⁾	--	<0.1	<0.1	
K+Na	ppm					1.0 max
V	ppm	⁽²⁾	--	<0.1	<0.1	0.5 max

(1)NATO F-76 results are typical based on analyses conducted over several years by Code 859 CDNSWC, Annapolis.

(2)Trace metals shall be determined by whatever industry-accepted method – such as AA or ICP-AES – which affords the level of detection required. The producer shall specify the method used.

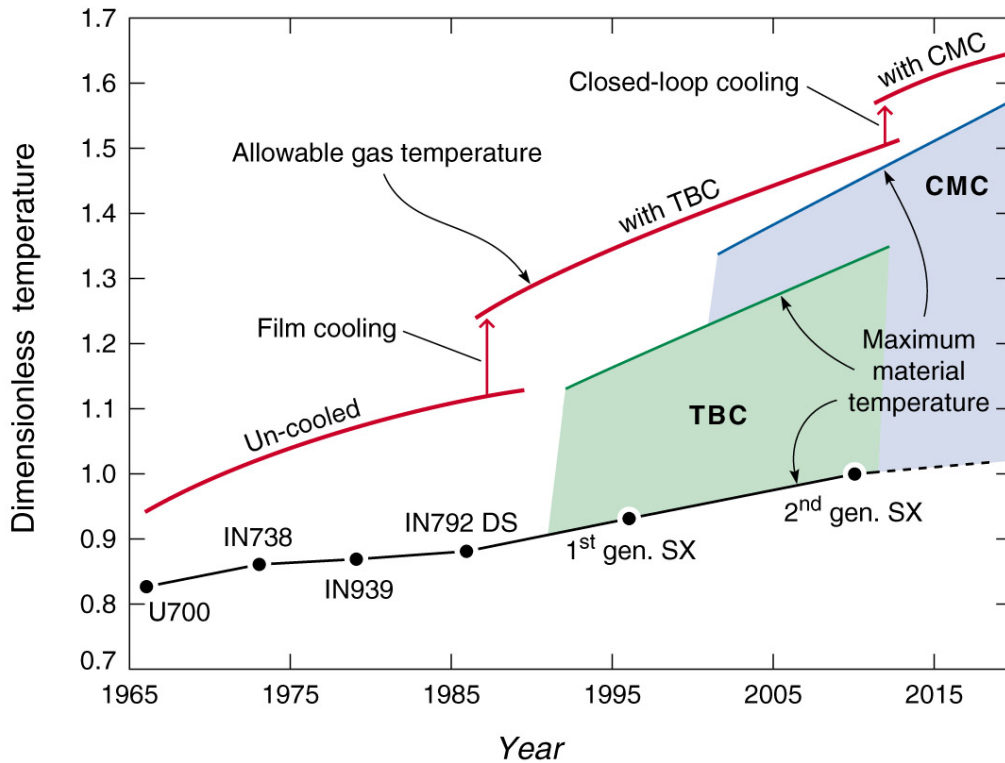


Figure 1 – Development of high temperature superalloys. Use of thermal barrier coatings and different cooling schemes have allowed continued use of superalloys. Future advances will require new high temperature materials.

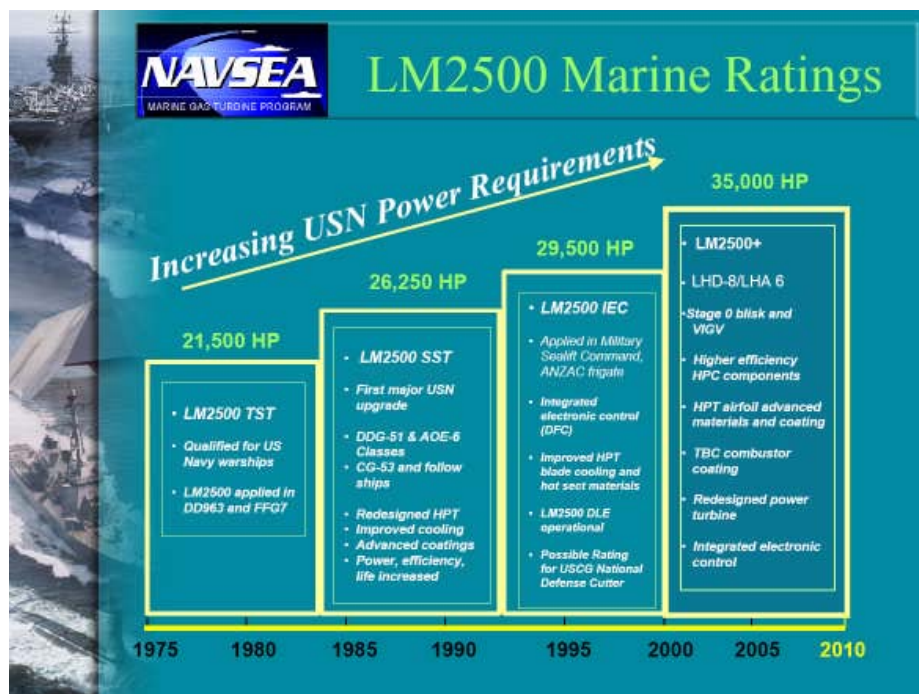


Figure 2 - U.S. power needs have increased 63% since 1975 due to greater power needs for weapons and operational systems [40].

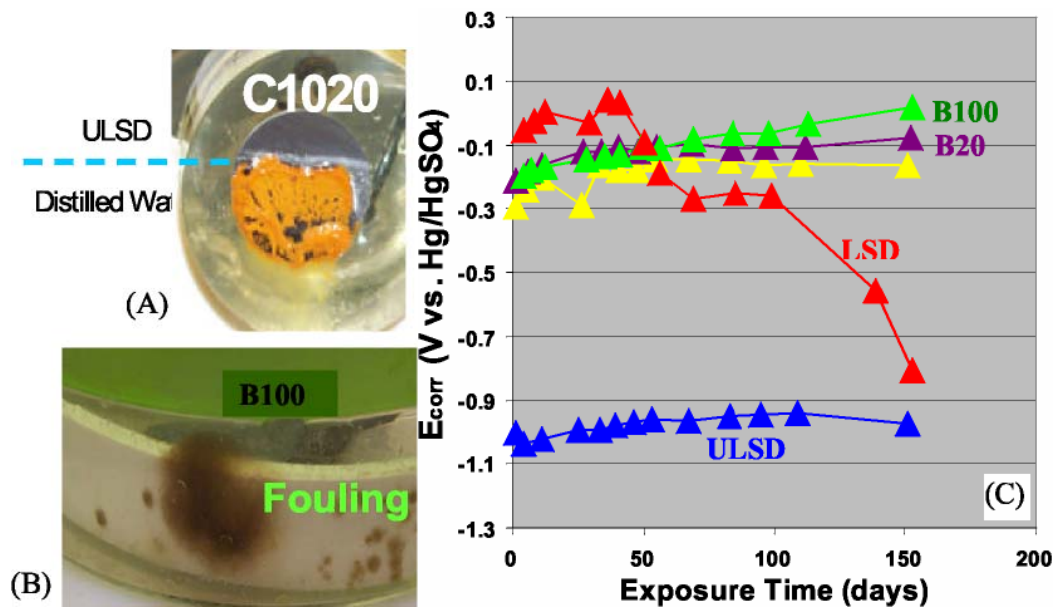


Figure 3 – In (A) AISI 1020 carbon steel shows corrosion at distilled water/ultra low sulfur diesel (ULSD) fuel interface after 4 days exposure. (B) exhibits biofouling in biodiesel (B 100). In (C) The approximately *1 Volt difference* in measured E_{corr} values across the different exposure conditions for C 1020 clearly demonstrates the differences in material/fuel mixture interactions for the different fuels (LSD – low sulfur diesel < 500 S; B20 (5% B 100/95% ULSD)). (Research by B. Little, J. Lee, NRL Stennis)