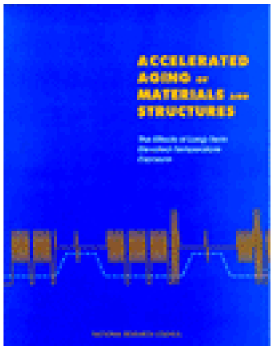

Accelerated Aging of Materials and Structures: The Effects of Long-Term Elevated-Temperature Exposure

Committee on Evaluation of Long-Term Aging of Materials and Structures Using Accelerated Test Methods, Commission on Engineering and Technical Systems, National Research Council

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ACCELERATED AGING OF MATERIALS AND STRUCTURES

The Effects of Long-Term Elevated-Temperature Exposure

Committee on Evaluation of Long-Term Aging of Materials and Structures Using Accelerated Test Methods
National Materials Advisory Board
Commission on Engineering and Technical Systems
National Research Council

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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Finally, the committee gratefully acknowledges the support of Thomas E. Munns, National Materials Advisory Board Senior Program Officer, and Aida C. Neel, National Materials Advisory Board Senior Project Assistant.

Preface

A fundamental understanding of the physical phenomena associated with damage and failure must be developed to predict the response of a materials system to long-term exposure in a service environment. This can only be established by experimental materials characterization and development of the associated mathematical and computational models that describe the physical phenomena. While test methods and modeling codes are available to provide guidance on specific types of component design and test methodologies, these methods and models may require refinement and standardization.

The National Aeronautics and Space Administration requested the National Research Council's National Materials Advisory Board (NMAB) to identify issues related to the aging of advanced materials and suggest accelerated evaluation approaches and analytical methods to characterize the durability of future aircraft materials and structures throughout their service lives. An NMAB study committee was established to (1) provide an overview of long-term exposure effects on future high-performance aircraft structures and materials; (2) recommend improvements to analytical methods and approaches to accelerate laboratory testing and analytical techniques to characterize and predict material responses to likely aircraft operating environments; and (3) identify research needed to develop and verify the required testing, predictive analytical capabilities, and evaluation criteria.

The committee chose to examine the issues of long-term aging of materials and structures by examining candidates being considered for use on a future High-Speed Civil Transport as a case study.

The committee hosted a Workshop on Long-Term Aging of Materials and Structures, which was held at the National Academy of Sciences on August 10–12, 1994. Workshop attendees included representatives from industry, government, and academia. The results of this workshop served as an important resource for the preparation of the committee's report.

Comments and suggestions that readers of this report wish to make can be sent via Internet electronic mail to nmab@nas.edu or by FAX to the National Materials Advisory Board (202) 334-3718.

Edgar A. Starke, Jr.,
Chair Committee on Evaluation of Long-Term
Aging of Materials and Structures Using
Accelerated Test Methods

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Executive Summary

The characterization of long-term responses of materials and structures to complex or cyclic environmental conditions presents a difficult challenge to those involved in materials selection and structural design. The problem is particularly challenging when the required service life is inordinately long compared with the time available for development and evaluation of materials and components. In most cases, service failures due to inaccurate characterization of aging responses result in potentially costly repair or premature component replacement. However, in safety-critical applications such as nuclear reactors and commercial aircraft the cost of inaccurate characterizations could be significantly greater.

Simulated service testing to characterize materials aging is fraught with deficiencies that stem from the inability to reproduce complex service conditions in the laboratory. Important aspects of the environmental conditions encountered in service cannot be accurately simulated. These environments are influenced by changing loads, temperature, humidity, radiation, and other effects that are interactive and cannot be consistently recreated and controlled. Moreover, critical degradation mechanisms and failure modes are not well known and understood prior to testing. While most service simulation testing has provided insights concerning degradation mechanisms and potential failure modes, it has yielded little engineering-quality data useful in the systematic characterization of materials aging. Thus, alternative approaches are required to develop such data.

The National Aeronautics and Space Administration (NASA) requested that the National Materials Advisory Board (NMAB) of the National Research Council identify issues related to the aging of materials and suggest accelerated evaluation approaches and analytical methods to characterize the durability of future aircraft structures throughout their service lives. The NMAB formed a committee to (1) provide an overview of long-term exposure effects on future high-performance aircraft structures and materials; (2) recommend improvements to analytical methods and approaches to accelerate laboratory testing and analytical techniques to characterize and predict material responses to likely aircraft operating environments; and (3) identify research needed to develop and verify the required testing, predictive analytical capabilities, and evaluation criteria.

The committee has examined the problem of aging characterization using the expected conditions and candidate structural materials for the High-Speed Civil Transport (HSCT) as a case study. The HSCT is a potential long-range supersonic commercial transport being considered by the aircraft industry for introduction early in the next century. The HSCT provides an important and instructive example because (1) the HSCT will be operated in a complex and severe service environment compared with current subsonic aircraft; (2) a broad range of materials with potentially different degradation mechanisms are being considered for structural applications; and (3) the development of the HSCT could be critical to the future commercial aircraft market for the U.S. aircraft industry well into the next century.

The committee believes that an approach based on a more fundamental understanding of materials response, degradation methods, and models and simulations using validated accelerated test methods will lead to increased confidence in aging predictions. In this light, the committee has recommended such an approach to aging characterization and has identified the critical research and data needs.

MATERIALS AGING CHARACTERIZATION

The committee recommends that, regardless of the material or application, the fundamental approach to the characterization of aging behavior should be the same. The approach that the committee recommends involves five steps. These steps are the basis for organizing the committee's conclusions and recommendations. The steps required to characterize the aging responses of materials and the evaluation of structures include:

- defining the service environment,
- identifying probable degradation or failure mechanisms,
- characterizing the materials aging responses using accelerated methods and analytical models,
- using test and model results to analyze and understand aging in structural components, and
- validating predictions.

As a general finding, the committee determined that several organizations have important roles in the characterization of materials aging in high-speed aircraft applications. The aircraft manufacturers should define the service conditions and data needs, apply analytical techniques to predict the aging responses at the component level, and validate predictions against controlled real-time tests. The material suppliers and academic researchers should perform the systematic characterization of materials properties and aid in the identification of potential degradation mechanisms under the full range of service and test conditions. The committee recommends that:

- NASA (1) integrate the efforts to provide fundamental characterization of materials properties, degradation mechanisms, and aging responses; and (2) develop the modeling capability to relate aging responses to component performance.

Service Environment

The service environment must be defined as precisely as possible to characterize the aging of a material or structural component. This can prove very difficult for application of materials under environmental conditions that differ significantly from previous experience. This difficulty arises because actual data are scarce, and conditions are defined by the component manufacturer largely through estimates or analysis. Among the variables that must be considered for the high-speed aircraft applications are operating temperatures, loads, ambient environmental conditions, moisture and fluid exposures, radiation, maintenance, and ground handling.

- The committee recommends that airframe and engine manufacturers, with assistance from NASA, continue to improve their understanding of the service environment expected for future high-speed aircraft. Emphasis should be placed on the analysis of aerothermal and chemical interactions and heat transfer to better define component temperature and thermal gradients and on characterization of ambient exposure conditions throughout the typical flight regimes.

Materials and Degradation Mechanisms

The properties of the aluminum alloys, titanium alloys, nickel-based superalloys, and ceramic-matrix and polymermatrix composites that are candidate materials for high-speed aircraft structures and engines degrade with time when exposed to elevated temperatures. Designers of high-speed commercial aircraft will use physical and mathematical models to characterize long-term behavior of candidate materials. This process requires the designers to continually build on their understanding of the degradation and damage accumulation mechanisms and to improve models used in the analysis of materials properties.

The evaluation of basic materials properties and definition of critical degradation mechanisms for the candidate structural materials is, at present, incomplete. The scarcity of available property data constrains the analysis of aging responses.

- The committee recommends that NASA emphasize fundamental work to characterize materials properties and, most important, to determine critical degradation and damage accumulation mechanisms over a broad range of environmental conditions. This work should allow determination of the mechanisms that are likely to have the greatest influence on component durability.

Characterization of Aging Responses

Once the fundamental materials properties have been defined and the probable degradation and damage mechanisms established, the response of the material to service conditions can be estimated with greater confidence. The characterization of aging responses in structural materials entails establishing the fundamental relationships between service and environmental exposure and structure and property metrics. To be useful in analytical models, the relationship between exposure and material structure or property must include methodologies to integrate degradation rates; dependence on environmental factors such as temperature, pressure, loads, or concentrations of chemical agents; and the effect on significant structural design or performance metrics.

Methods to evaluate fundamental materials responses are fairly well established for specific damage mechanisms acting alone. However, the potential for synergistic effects among mechanisms is not completely understood. Unfortunately, it would be virtually impossible to explore each possible combination. Therefore, a carefully designed evaluation approach using statistical design of experimental techniques is required to determine the interactions with the greatest potential effects on in-service properties.

A critical aspect in the testing and characterization of aging response is the relation to a performance metric (most often related to mechanical properties). Degradation mechanisms can operate over a broad hierarchy of size scales, ranging from intermolecular to macroscopic, and time scales ranging from seconds to years. It is important to test aging response at the scale where the degradation takes place. For example, oxidation of polymeric composites has the most profound effect at edges and at fiber-matrix interfaces. Hence, the most sensitive measure of oxidation effects would be the degradation of the strength of the bond between the fiber and matrix resin.

The committee recommends that:

- Methods be developed to characterize aging responses in structural materials for previously identified degradation mechanisms by establishing the fundamental relationships among service and environmental exposure conditions, damage accumulation, and structure and property metrics. These relationships must include property degradation or damage accumulation rates; dependence on critical environmental factors such as temperature, pressure, loads, strain rate, concentrations of chemical agents, and synergistic effects; and effects on significant performance metrics.

- Statistical experimental design approaches be used to establish critical dependencies between degradation mechanisms.

Accelerated Methods

The long service-life requirements of high-speed commercial transports and the limited time available for development, evaluation, and validation of material candidates makes acceleration of aging characterization methods necessary. Methods include accelerated testing and accelerated aging. *Accelerated testing* to reduce the time required for testing material responses is required for mechanisms that involve progressive accumulation of damage or deformation that could lead directly to failure. Examples in which accelerated testing is required include creep and high-temperature fatigue. For accelerated test methods it is important to establish the equivalence between test progression and service exposure time or flight cycles. To reduce the time required to expose materials to aging conditions, *accelerated exposures*are used to generate end-of-life microstructure or damage states for subsequent characterization tests. An example in which an accelerated exposure is required is coarsening of metal alloy microstructure, which would be expected to affect strength and toughness after exposure.

For accelerated aging, the calibration of test progression with service exposures is not as critical as the confidence that the microstructural features, produced using accelerated exposure methods, represent realistic end-of-life conditions. In cases that involve multiple interacting damage mechanisms (e.g., thermomechanical fatigue), both accelerated aging and accelerated testing could be required.

Accelerated exposures and testing can be accomplished through a number of schemes, depending on the aging mechanisms and the environmental variables. In many cases, it may be possible to accelerate exposures or tests by increasing temperature and loads, predamaging test articles, shortening hold times on cyclic exposures, or increasing the concentration of a degradative chemical or compound. When using accelerated exposures, it is necessary to anticipate and avoid excursions into or near regimes where other degradation mechanisms are expected to become active.

Accelerated methods become much more complex when multiple mechanisms and synergistic effects are involved because the relationship between accelerated and service conditions is not usually the same for different mechanisms. For this reason it is very difficult to directly test multiple accelerated conditions simultaneously. The committee concludes that the most viable approach to the characterization of multiple aging mechanisms is to incrementally subject samples to accelerated conditions designed to advance single-failure mechanisms. Samples would be cycled through a series of conditions designed to advance different discrete mechanisms, in turn, until end-of-life conditions are reached.

The committee recommends development of:

- Accelerated exposure and test methods, with calibration to service conditions or end-of-life microstructural conditions, for critical degradation mechanisms.
- Testing and exposure approaches that allow incremental application of conditions to evaluate multiple, synergistic degradation mechanisms.

Analysis of Structures

Modeling techniques are valuable in the process of understanding the fundamental aging characteristics of materials and the properties of the structural components fabricated from them. The effects of scale, geometry, surface quality, coatings, and individual service conditions must be considered in the formulation of models. Analyses can also be done of mechanisms and rates of degradation at increasing size scales to provide technical guidance for component design and testing protocols.

The potential degradation of mechanical properties as determined from materials aging-response characterizations and the potential for damage accumulation over the service life must be considered when developing design property test programs and protocols for structural components. Durability predictions can be verified by comparing model predictions with controlled real-time and accelerated laboratory exposure and test methods. Validation of service condition assumptions, characterization test results, and model predictions can be accomplished based on visual and nondestructive monitoring of fleet-leading aircraft and mechanical and microstructural evaluation of components returned for service.

The committee recommends that:

- An integrated modeling capability be developed to relate characterizations of materials aging responses to component performance. An ability to examine the effects of scale, geometry, finishes, and individual service conditions must be part of the model specifications.
- Property degradation and damage accumulation be included as part of component durability evaluations and be considered in the design property test programs and protocols.

- Model predictions be verified using controlled real-time tests and accelerated exposure and test methods.

REPORT ORGANIZATION

The findings of the committee have been organized into five chapters. Chapter 1 introduces the study task and report objectives. Chapter 2 describes the service or operating environment expected for airframes and engines expected to be used in future high-speed aircraft. Chapter 3 identifies and describes the candidate structural materials for such aircraft applications. Chapter 4 describes critical degradation mechanisms for the various candidate materials. Chapter 5 describes accelerated methods for the characterization of aging of materials and structures and describes the approach to materials aging recommended by the committee.

1

Introduction

AGING OF MATERIALS AND STRUCTURES

To predict the response of a materials system to long-term exposure in a aircraft structures service environment, a fundamental understanding of the physical phenomena associated with damage and failure must be developed. This can only be established by experimental materials characterization and development of the associated mathematical and computational models that describe the physical phenomena. In many cases, testing standards and codes are available to provide guidance on specific types of component design and test methodology. However, for some advanced materials (e.g., composites) different approaches to materials testing may be required, and there may be a lack of standardized methods. Although the requirement for the same basic material properties may be similar, users often develop their own test methods. The different testing methodologies can lead to ambiguities in the test data, resulting in uncertainties in materials selection, design, and production.

The evaluation of long-term aging responses of materials and structures using accelerated testing and analytical methods is very difficult, especially for the complex conditions encountered in aircraft service. Even the best techniques will probably not yield completely satisfactory predictions of materials performance. However, because new aircraft will be designed, and materials and structures evaluated over their entire life cycle, it is important to develop testing and analysis methods that provide the best possible understanding of materials and structures performance to support materials selection and structural design decisions. It is better to have incomplete data available in time to influence key program decisions than to wait for the completely rigorous data to be developed.

Concerns over these issues have led the National Aeronautics and Space Administration (NASA) to request the National Research Council's National Materials Advisory Board (NMAB) to identify issues related to the aging of advanced materials and suggest accelerated evaluation approaches and analytical methods to characterize the durability of future aircraft materials and structures throughout their service lives. An NMAB study committee was established to (1) provide an overview of long-term exposure effects on future high-performance aircraft structures and materials; (2) recommend improvements to analytical methods and approaches to accelerate laboratory testing and analytical techniques to characterize and predict material responses to likely aircraft operating environments; and (3) identify research needed to develop and verify the required testing, predictive analytical capabilities, and evaluation criteria. The committee emphasized methods to evaluate materials performance and long-term aging responses and methods to develop property relationships for component design. Methods to evaluate specific design details such as part geometry, joint design (bonded, welded, or fastened), or method of manufacture are not considered within the scope of this report.

Aging of current commercial and military aircraft has become a major concern as many older aircraft reach their original design life. Significant work is being accomplished by the aircraft industry, NASA, and the Federal Aviation Administration in this area, with emphasis on corrosion, widespread fatigue damage, and nondestructive evaluation methods to monitor the aging fleet. This report, however, considers long-term aging in the context of materials selection, materials evaluation, and component design for new systems. The emphasis is on new systems that will be subjected to sustained elevated-temperature environments. The goal is to provide the framework to develop sufficient and accurate scientific information such that aging issues can be predicted and considered in the design process. The ability to understand and predict aging processes can have immediate implications for dealing with existing fleets.

The committee chose to examine issues involved in the evaluation of long-term aging of materials and structures being considered for use on a future High-Speed Civil Transport (HSCT) as a case study. The HSCT provides a valuable case study because the anticipated service conditions are harsh, with severe combinations of thermal, environmental, and stress conditions. Despite the complexity involved, a substantial amount of work has been undertaken by airframe manufacturers and NASA to define service conditions in terms of flight profiles and to establish structural design criteria. A wide range of candidate materials are being considered, including high-temperature alloys, composites, and hybrid structures. Most important, consideration of aging issues for the HSCT represents an important need. The HSCT is considered critical to the future competitiveness of the U.S. aircraft industry, and much work is being undertaken to develop and understand materials for this important application.

CASE STUDY: HIGH-SPEED CIVIL TRANSPORT

The HSCT is a potential long-range, supersonic commercial aircraft being considered by the aircraft industry for introduction early in the next century. The development goals of the HSCT—5,000-nautical-mile range, approximately 300-passenger payload capacity, greater than Mach 2 speed at cruise, and ticket costs competitive with subsonic aircraft—represents a substantial improvement in capability over the existing technology (e.g., the Concorde) (Brunner, 1994; Grande, 1994).

The development of an HSCT poses challenges to the aircraft design community unlike any faced before in commercial aviation. New and future federal and international regulations will require that the aircraft meet strict noise and emission requirements in order to protect earth's fragile environment. In addition, service conditions during extended supersonic cruise are significantly more severe compared with those experienced by subsonic aircraft, supersonic fighters, or even the Concorde. Advanced materials and structural concepts for both the engine and the airframe are critical to the performance and economic viability of an HSCT.

Lightweight structural materials with long-term resistance to thermomechanical fatigue, creep, and environmental degradation in temperature ranges between 100 and 200 °C (212 and 392 °F) for the airframe (and much higher for the engine and for limited areas of the airframe) are needed to attain the speed, payload, and range necessary for an economically successful aircraft.

Candidate materials for the many different structural applications include polymer-matrix composites (both thermoplastics and thermosets), high-temperature and low-density aluminum alloys and aluminum-matrix composites, and improved titanium alloys for airframe applications and nickel-based superalloys and ceramic-matrix composites for engine applications. Also of great importance to the viability of future HSCT are support materials, including coatings, seals and sealants, adhesives, and fasteners and joining methods. These structural components will be complex, including bonded honeycomb constructions and dissimilar materials combinations produced using advanced joining methods and manufacturing processes. The final design must meet certification requirements for twice the proposed life-time of the aircraft (i.e., 120,000 hours for the airframe and 20,000 [1] hours for the engine). This requires a thorough understanding of the long-term material properties and anticipated failure mechanisms as well as component reliability and durability evaluation methods.

Due to the severe exposures and long service life projected for an HSCT, the time required for complete, real-time evaluation of thermomechanical aging in advanced materials and structures will not be available. Unfortunately, it is difficult to characterize time-dependent phenomena related to materials aging in accelerated tests and to predict the equivalent real-time behavior with a high degree of confidence, especially when multiple aging processes and degradation mechanisms are involved. Existing methods for accelerated service simulation testing and damage accumulation rules may be inadequate for analyzing complex structures operating in new environments.

There has been considerable work associated with the NASA High-Speed Research program and at the aircraft and engine manufacturers to characterize the performance of HSCT-candidate materials under expected service conditions (Brunner, 1994; Williams and Johnson, 1994). These efforts have provided important progress toward understanding the behavior of advanced materials under severe conditions and in identifying degradation mechanisms discussed in this report.

To provide a better understanding of the problem, the committee addresses the following concerns:

- What are the issues related to the performance of advanced materials over extended periods of time?
- What are the current methods for evaluating long-term aging responses of materials and structures, and how appropriate are they, considering the in-service conditions under which the HSCT must operate?
- What testing and analytical methods should be used to predict the performance of high-speed aircraft structures throughout their service life?
- What research should be initiated to develop and validate the necessary methodology for accelerated aging of materials and structures?

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[1] There has recently been an effort to extend design life for subsonic commercial engines to 30,000 hours. If adopted, this criterion would likely apply to the HSCT.

2

Aircraft Operating Environment

The first step in characterizing the aging of a material or structural component is to define the operating environment as precisely as possible. For new applications, this proves very difficult, since actual data are scarce and conditions are defined largely through estimates or analyses. Among the variables that need to be considered for the HSCT (High-Speed Civil Transport) are operating temperatures, loads, ambient environmental conditions, moisture and fluid exposures, radiation, maintenance, and ground handling. This chapter describes the factors that influence service conditions of supersonic, commercial aircraft. Some of the experience gained from the Concorde is described, followed by a discussion of the key variables that need to be considered to determine conditions expected for the HSCT.

THE CONCORDE EXPERIENCE

The typical mission of the Concorde, a long-range (trans-Atlantic) flight profile involving sustained cruising speed above Mach 2.0, was described by Harpur (1968). Like subsonic aircraft, the Concorde experiences variations in stress and temperature during flight; however, the airframe temperature variations are much more significant than for subsonic aircraft due to the effect of aerodynamic heating at supersonic speeds.

The skin temperature drops initially as the aircraft climbs due to exposure to decreasing ambient air temperatures. As the speed increases above about Mach 1, where the temperature begins to increase, the skin temperature reaches a maximum of 120°C (248°F) after exposure while cruising at Mach 2.2. (At Mach 2.0, the skin temperature would stay below 100°C (212° F); at Mach 2.4, it would reach 150°C (302°F.) During descent, the reverse occurs. Significant stresses also occur in supersonic aircraft because of thermal variations. Differences in temperature throughout the structure cause different parts of the structure to expand by different amounts, giving rise to thermal stresses which are added to the other imposed stresses. Figure 2-1 shows the predicted, maximum external surface temperature of the Concorde due to aerodynamic heating. Figure 2-2 shows a thermal profile due to exposure for a complete Concorde flight cycle.

Superimposed on this once-per-fright thermal cycle are stress variations. Once per flight, there is stress variation due to cabin pressurization and depressurization, as well as stresses that occur during take-off and landing. In addition, there are stresses due to maneuvering and gusts, but these are not expected to be as significant to supersonic aircraft as they are to subsonic aircraft.

HSCT CONDITIONS

Ground Exposure

Two types of ground exposure that must be considered are ambient environmental conditions and the potential for

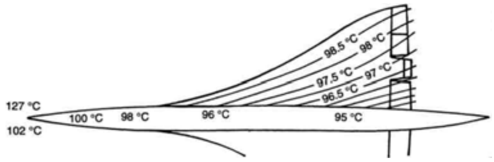


FIGURE 2-1 External structural temperature during cruise for the Concorde. Source: Peel (1994). © British Crown Copyright, 1971, Defence Evaluation and Research Agency. Reproduced with permission of the Controller, Her Britannic Majesty's Stationery Office.

damage caused by maintenance and repair actions as well as handling (or mishandling) considerations.

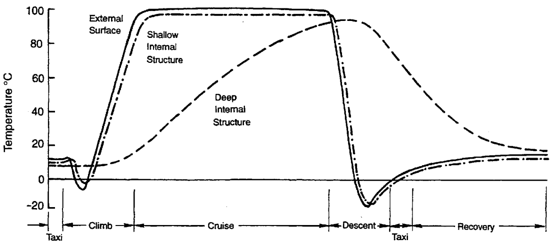


FIGURE 2-2 Structural temperature for a typical flight of the Concorde. Source: Peel (1994). © British Crown Copyright, 1971, Defence Evaluation and Research Agency. Reproduced with the permission of the Controller, Her Brittannic Majesty's Stationery Office.

Ground ambient exposure for commercial and military aircraft have been studied extensively (McCarty and Wilson, 1983). Exposure to extremes in temperature (ranging from about 60°C to −30°C [140°F to −22°F]), moisture (extreme humidity to desert conditions), and radiation (especially ultra-violet) can cause degradation of coatings and structural materials or exacerbate the damaging effects of flight exposure conditions.

Discrete damage events, both on the ground and in flight, represent a threat to polymeric composite and thin-skinned components. Sources of discrete damage include hail impact, lightning strike, transport and handling, and foreign objects (Blohm, 1994).

Airline maintenance operations can also have a profound effect on materials aging. The integrity of finish systems or of delicate minimum-gauge components can be degraded due to airline maintenance and servicing operations. A study by IATA (1991) indicated that as much as 40 percent of aircraft damage requiring repair is due to ramp and maintenance damage from such sources as catering equipment and personnel, baggage loaders, lavatory and potable water service, and jetway interfaces. Chemicals encountered in aircraft servicing, including cleaning fluids, fuel, de-icing and anti-icing fluids, paint strippers, and hydraulic oils, need to be identified and the effect on finishes and components assessed.

Another consideration is the integrity of repairs that are made to structural components during airline service. Most aging models assume that the structure would remain in

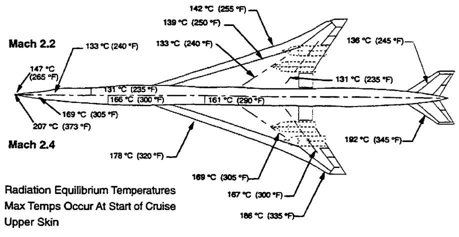


FIGURE 2-3 Predicted equilibrium skin temperatures for a Mach 2.2 and Mach 2.4 HSCT. Source: Brunner (1994).

as-fabricated condition. Since in-service damage and subsequent repairs are inevitable, the effect of in-service repairs should to be considered.

Flight Exposure

Airframe

In general, the most severe service conditions are encountered during flight. For supersonic aircraft, the flight-cycle conditions are determined by speed at cruise, altitude, flight loads, and spike (or failure) conditions. The HSCT will be designed for a lifetime of approximately 20,000 flight cycles, which for a typical service cycle represents about 60,000 flight hours (Brunner, 1994). A substantial portion of this flight cycle will be under supersonic cruise conditions at speeds between Mach 2 and Mach 2.4.

The expected flight cycle for the HSCT will be similar to the Concorde cycle described earlier in this chapter, except:

- higher speeds at cruise will necessitate higher cruise altitudes, and
- the significantly greater range will result in longer typical times at cruise conditions.

Higher cruise altitudes will result in a less oxidative environment due to reduced atmospheric pressure (and correspondingly lower oxygen concentration) as altitude increases. Since there has been little work in characterization of highaltitude environments, progress is needed to better define these conditions.

The HSCT flight cycle imposes a range of thermal environments on structures. As observed for the Concorde, subsonic climb and cruise conditions lead to reduced temperatures due to lower ambient temperatures as the altitude increases. Structures on current commercial aircraft are generally designed to withstand low-temperature exposures to −54°C (−65 °F).

The most severe service conditions for the HSCT are the high-temperature exposures due to the aerodynamic heating that results from supersonic cruise. The highest temperatures occur at the leading edges of the structure. Component temperatures increase significantly as speed increases. An estimate of HSCT surface temperature distribution is shown in Figure 2-3 for Mach 2.2 and 2.4 configurations. Surface temperatures are strongly dependant on altitude, angle of attack, radiation conditions, and surface emissivity of both bare and painted surfaces. To fully characterize thermal exposures, thermal and optical properties of the candidate structural materials and surface finishes as well as heat-transfer behavior characteristics must be understood.

In addition to mechanical load conditions encountered in flight, designers must also account for thermal expansion effects and thermal expansion mismatches between adjacent structures. Current methods can model expected loads, but the thermal environment and heat-transfer characteristics must be well understood to provide complete information.

Occasional thermal spikes may be encountered due to rapid descents. These conditions may result in the aircraft attaining speeds 10 percent higher than the design maximum with resulting effects on aerodynamic heating. The structure must be able to retain structural properties under these conditions without sustaining permanent damage. Response of materials subjected to thermal spike conditions (rapid heating, rapid loading) must be understood.

Engine

Flight conditions expected for the engines of the HSCT, as for the airframe, are more severe than current applications (Williams and Johnson, 1994). The expected temperatures in the combustor section are significantly higher than current subsonic engines—1540–1650°C (2800–3000°F) for the HSCT compared with approximately 1425°C (2600°F) for current commercial aircraft engines. The more-severe conditions are driven largely by design requirements for low NO_x emissions combustors and low-noise exhaust nozzles. The duty cycle for the HSCT engine also requires operation for a greater percentage of time at temperatures closer to maximum than current commercial or military engines. A comparison of HSCT and current commercial engine cycles is shown in Figure 2-4.

SUMMARY AND RECOMMENDATION

The expected service environment for the HSCT has been the subject of a significant amount of work by aircraft

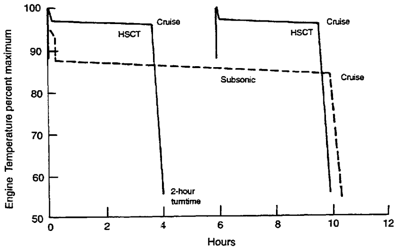


FIGURE 2-4 Comparison of HSCT and subsonic engine duty cycle for comparable 5,000 nm flights. Source: Williams and Johnson (1994).

manufacturers (Brunner, 1994; Grande, 1994). Understanding typical service conditions is also crucial to NASA efforts to establish goals and criteria for research in enabling HSCT technologies.

An accurate understanding of expected service conditions is crucial in the selection of structural materials, the identification of design criteria, and the testing and evaluation of structural concepts. Conditions for new applications are defined largely through estimates or analysis. Among the variables that must be considered for the high-speed aircraft applications are operating temperatures, loads, ambient environmental conditions, moisture and fluid exposures, radiation, maintenance, and ground handling.

- The committee recommends that airframe and engine manufacturers, with assistance from NASA, continue to improve their understanding of the service environment expected for future high-speed aircraft. Emphasis should be placed on the analysis of aerothermal and chemical interactions and heat transfer to better define component temperature and thermal gradients and on characterization of ambient exposure conditions throughout the typical flight regimes.

The range of thermal, mechanical, and environmental conditions described in this chapter and the complex interactions among them makes the HSCT an instructive case study in the examination of materials aging responses. The following chapter describes how, based on the HSCT conditions, materials candidates have been identified. Subsequent chapters discuss the evaluation and characterization of materials degradation and aging responses.

3

Candidate Materials

Aluminum alloys and aluminum-matrix composites, titanium alloys, and polymer-matrix composites are candidate materials for supersonic airframe structures, and nickel-based superalloys and ceramic-matrix composites are candidates for engine applications. To provide technical background for later discussions of degradation mechanisms and evaluation methods, this chapter describes the material candidates, important material properties, and the state of development toward high-temperature aircraft applications. Significant work is in progress to develop these material candidates into the materials that would be used to produce the High-Speed Civil Transport (HSCT) (as well as advanced subsonic aircraft). This chapter does not attempt to discuss every material that will be available, rather discussion is limited to candidate materials that are most likely for HSCT applications.

ALUMINUM ALLOYS

There are three classes of aluminum-based materials that were initially considered by airframe manufacturers for elevated-temperature high-speed aircraft applications:

- ingot metallurgy alloys (with or without lithium) (e.g., 2XXX-series alloys),
- non-heat-treatable dispersion-strengthened alloys (e.g., Al-Fe-X alloys), and
- discontinuously reinforced metal-matrix composites.

Ingot alloys and dispersion-strengthened alloys would be candidates for applications where strength and fracture toughness are critical (e.g., the fuselage and lower wing). The tensile yield strengths at room temperature following elevated-temperature exposure as a function of exposure temperature for several ingot alloys are shown in Figure 3-1.

Standard ingot alloys, such as those used for subsonic aircraft, typically have more favorable strength and toughness combinations than elevated-temperature aluminum alloys. For example, Figure 3-2 shows fracture toughness versus tensile yield strength for X8019 (Al-Fe-Ce) products and standard ingot (7XXX and 2XXX series) alloys, and X8019 products and elevated-temperature ingot metallurgy (2XXX series) alloys. Discontinuously reinforced aluminum-matrix composites would be candidates for applications where high stiffness is needed (e.g., the upper wing).

Ingot metallurgy alloys that are considered to be stable at elevated temperatures include Al-Cu, Al-Cu-Mg, and Al-Cu-Li-(Mg)-(Ag) alloys, including alloys such as 2219 and 2519 (Al2Cu strengthened) and 2618 (Al2CuMg strengthened). Precipitation provides the largest contribution to strength in these alloys. Precipitation strengthening relies on the increasing solubility of alloying additions in aluminum as the temperature increases. Therefore, elevated-temperature exposure may cause dissolution of some of the strengthening precipitates. Furthermore, since artificial aging of these alloys is typically done at temperatures not much higher than the upper range of high-speed aircraft service temperatures (e.g., 160– 190°C [320–374° F]), service exposures could cause overaging (coarsening of microstructure) and consequent strength losses. For this reason, 2XXX ingot alloys are not considered candidates where temperatures exceed 135°C (275°F).

Dispersion-strengthened Al-Fe-X alloys were initially considered by airframe manufacturers to be candidates for the fuselage and lower wing of a Mach 2.4 aircraft. These alloys, the most notable of which are Alcoa's Al-Fe-Ce alloy X8019

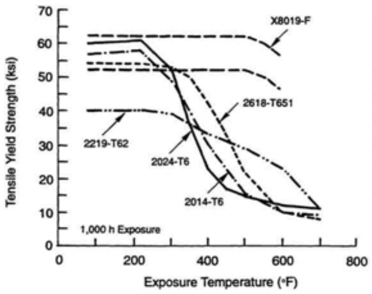


FIGURE 3-1 Tensile yield strength at room temperature versus exposure temperature for several ingot metallurgy 2XXX alloys and X8019 after 1,000 hours exposure. Source: Alcoa (1995).

and AlliedSignal's Al-Fe-V-Si alloy 8009, were particularly attractive because of their exceptional thermal stability. Both are strengthened by about 25-volume percent of fine intermetallic particles and a fine substructure which are maintained even after extended exposures at temperatures up to about 300°C (572°F) or higher. Unfortunately, the rapid solidification that is necessary to introduce the dispersoids leads to product-size limitations and high material costs. Furthermore, as these materials were considered for high-speed aircraft, several technical problems surfaced. Specifically, both materials exhibit losses in fracture toughness and ductility as the temperature is increased from room temperature to 150°C (302°F). Also, elevated-temperature fatigue resistance is poor and fracture toughness is extremely strain-rate sensitive.

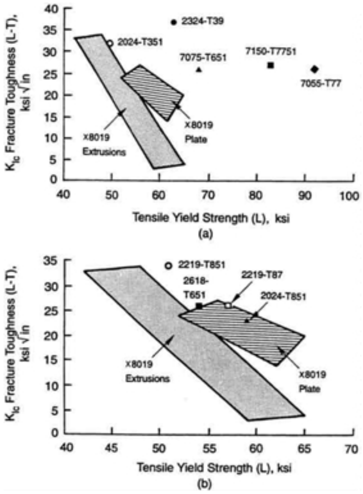


FIGURE 3-2 Fracture toughness versus tensile yield strength for (a) X8019 products and several ingot metallurgy alloys, and (b) X8019 products and several moderately elevated-temperature ingot metallurgy 2XXX alloys. Source: Alcoa (1995).

Discontinuously reinforced aluminum-matrix composites can be produced by conventional powder metallurgy methods and other means, including casting, spray deposition, and in situ casting techniques. If powder metallurgical processing is used, a precipitation-strengthened 2XXX alloy or a dispersion-strengthened Al-Fe-X alloy could be selected as the composite matrix. By incorporating reinforcements, significant increases in elastic modulus and modest improvements in strength can be achieved.

TITANIUM ALLOYS

The high-temperature-strength retention of titanium alloys is considerably better than aluminum alloys. Therefore, titanium alloys are candidates for application in components where service temperatures exceed 135°C (275°F). For application in advanced aircraft, titanium alloys must have improved combinations of strength, toughness, elastic modulus, and density, as well as processability at an affordable cost. Property goals have been established for titanium alloys for application on a Mach 2.4 HSCT (Brewer and Curtis, 1994). These include goals for high-strength, high-toughness, and high-modulus alloys. Figure 3-3 shows these goals with respect to the toughness and modulus as a function of specific strength for several current titanium alloys.

Three titanium alloys are emerging as prime candidate materials for a Mach 2.4 aircraft:

- A low-cost beta alloy, TIMETAL LCB (Ti-6.8Mo4.5Fe-1.5Al-0.09O, by weight percent), is a prime candidate for high-strength applications.
- A near-beta alloy, Beta-CEZ (Ti-5Al-4Mo-4Zr-2Sn2Cr), developed in France for superplastically formed turbine disks, is a prime candidate for high-toughness applications. An alternative for high toughness is Ti-622-22 (Ti-6Al-2Sn-2Mo-2Zr-2Cr), an alpha-beta alloy similar to Ti-6Al-4V.
- An alpha-beta alloy, TIMET 62S (Ti-6Al-2Fe), is being considered for the high-stiffness applications.

Beta titanium alloys contain elements that stabilize the body-centered-cubic beta phase (e.g., molybdenum, vanadium, tungsten, niobium, iron, chromium, and silicon) while precluding the formation of brittle martensitic products of beta transformation. A microstructure for high strength is produced by solution heat treatment, air cooling to 25°C (77°F; retaining all beta), and aging to produce a substantial volume fraction of the hexagonal-close-packed alpha phase in a continuous beta matrix. Such alloys offer an excellent combination of high strength, modest density, and formability, as well as good corrosion and fatigue resistance. The practical increase in strength is limited by concomitant decreases in ductility and toughness (Kawabe and Muneki, 1993). Homogeneous and fine precipitation of the alpha phase (as well as other metastable phases) produces the optimum strengthening effect. In addition, transient phases and brittle eutectoid compounds may form depending on alloy composition, processing history, and, in some cases, service conditions. For example, Beta-CEZ contains two eutectoid stabilizers, chromium and iron, that could favor the precipitation of $TiCr_2$ and TiFe intermetallic compounds, with a consequent decrease in ductility (Vassel, 1993). The omega phase forms in some beta alloys at low aging temperatures; although the omega phase has a high strengthening effect, it degrades ductility. Omega phase has been detected in the low-cost beta alloy after short-term aging below 400°C (752°F; Rack, 1994).

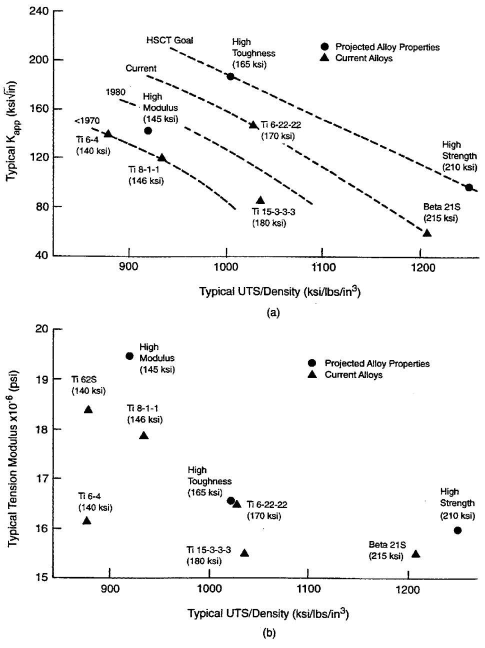


FIGURE 3-3 (a) Fracture toughness and (b) elastic modulus of candidate titanium alloys as a function of normalized strength (strength/density). Source: Brewer and Curtis (1994).

SUPERALLOYS

Nickel-based superalloys are chemically complex alloys with a combination of high-temperature strength, resistance to environmental degradation, toughness, and fatigue resistance not available in any other current alloy system (Sims, 1986).

Nickel-based alloys are strengthened by incoherent phase formation and solid solutions. Superalloys retain high strengths at elevated temperatures through the precipitation of a coherent (gamma-prime) phase. The result is a family of alloys capable of operating at greater than 90 percent of their melting temperature, making nickel-based alloys the favored alloys for use in turbine-engine rotating components. These alloys are also widely used in nonrotating structures, such as the engine case, vane, and combustor.

The most important developments for nickel alloys have been made possible through the development of investment casting processes. This development has resulted in the ability to cast directionally solidified and single-crystal components that include complex, cast-in, internal air-cooling passages. The significance of this accomplishment is that the combination of sophisticated cooling and single-crystal alloys has achieved an increase in temperature capability of greater than 80°C (144°F) over conventional castings.

Component design engineers seek to mitigate the impact of the operating conditions on component integrity. One approach has been to rely on coating technology to appreciably extend the service lifetime of nickel alloys (NRC, in press). Another approach has been the use of active component cooling to significantly decrease the steady-state temperatures. Both of these approaches have become essential to the design of hot-section components. Advanced turbines, for example, have combustion gas temperatures in excess of the incipient melting temperatures of the superalloy components. Such designs are being implemented through extensive use of component cooling (Stringer and Viswanathan, 1990).

POLYMER-MATRIX COMPOSITES

Polymer-matrix fibrous composites, primarily because of their high specific strength and stiffness, have found increasing application in aircraft structures. The critical need for significant weight savings, design flexibility, and extended flight efficiency for advanced aircraft such as the HSCT has focused attention on composites for high-temperature applications.

Polymeric composites that are candidates for application in high-temperature aircraft structures consist of high-strength, intermediate-modulus carbon fibers (e.g., Hercules IM7, Toray T-800H) embedded in a high-temperature-resistant polymeric matrix. Glass and high-modulus, carbon-fiber-reinforced composites may also find application in the HSCT. Two main categories of matrix materials are thermosets and thermoplastics. Matrices with varying high-temperature capability can be found in either category.

Thermoset Matrices

Thermosetting polymers are crosslinked polymer networks that, on completion of forming and curing, are considered infusible and incapable of being reshaped. The most common high-temperature (T > 132°C [270°F]) thermosets are cyanate esters, benzocyclobutene, bismaleimides (BMIs), and crosslinked polyimides such as PMR-15 (Brunner, 1994). They are relatively brittle, resulting in low fracture toughness; reduced damage tolerance; and lower transverse tensile, interlaminar tensile, and in-plane shear failure strains. High-temperature thermosets are also prone to microcracking during processing and when subjected to mechanical loading or thermal cycling. Thermosets offer advantages over thermoplastics in ease of processing, addition polymerization with little or no evolution of volatiles, high creep resistance, good fluids resistance, and low resin costs.

Significant effort, particularly with the BMIs and cyanate esters, has focused on developing toughening mechanisms through the addition of a discrete second phase. Although improvements in impact tolerance and toughness have been attained, other properties have been compromised. In general, toughened BMIs exhibit lower stiffness, complications in processing multiphase systems, a degradation in mechanical properties, and higher costs.

Thermoplastic Matrices

A wide variety of high-temperature thermoplastics have been introduced, including polyimides, polyamideimides, polysulfones, and polyetherketones (PEEK, PEKK). Thermoplastics are linear polymer arrays with amorphous, semicrystalline, or mixed morphology. Limited crosslinking through reactive end-groups may be introduced in some polymers in the latter stages of processing. Crosslinking can provide additional temperature and chemical resistance, but with a resultant compromise of thermoplastic characteristics including formability and toughness.

Thermoplastics typically exhibit excellent toughness, high damage tolerance, good mechanical properties, and excellent shelf life. However, chemical resistance is lower, susceptibility to creep deformation is increased, and resin costs are higher than for thermosets. The development of crystalline morphology imparts solvent and fluid resistance because the close-order intermolecular packing resists the diffusion process. Added benefits of crystallinity are lower solvent-induced stress cracking and increased modulus. The development of crystalline morphology requires reproducible control of the cool-down process to permit the necessary polymer mobility needed for crystalline growth. Phase boundaries in crystalline thermoplastics also represent stress discontinuities which may compound the failure process, particularly under hot and wet conditions where the amorphous regions will have a higher affinity for moisture.

High molecular weights common in high-temperature thermoplastics result in high melt viscosity and low flow in the matrix that can make processing difficult. The high melt viscosity can restrict uniform fiber wet-out during material fabrication, and consolidation into high-quality structure requires high pressures and temperatures that lead to high processing costs. Processing thick-section structures containing flanges or other complexities make control of the time-temperature-process history even more critical to both general quality and the formation of any desired crystalline morphology. Poor management of volatiles generated from solvent or polymer condensation reactions can also produce voids in the composite, degrading the mechanical properties of the material.

CERAMIC-MATRIX COMPOSITES

The principal potential applications for ceramics and ceramic-matrix composites in the HSCT are in the engine combustor and the high-temperature parts of the exhaust nozzle. In the combustor, in addition to the high operating temperature (up to 1300°C [2372°F]), the materials must resist both fuel-rich and fuel-lean environments. High thermal stress resistance is required because of the steep thermal gradients through the thickness of the combustor wall and the transients during operation. The materials must be damage tolerant and resist vibrational stresses (fatigue). In the nozzle, the requirements are similar but the thermal stress resistance requirement is relaxed—the environmental resistance and the fatigue resistance are key durability issues in the nozzle as well as in the combustor.

Since damage tolerance is required and catastrophic failure cannot be tolerated, ceramic-matrix composites are required rather than monolithic ceramics. Unfortunately, high-temperature ceramic-matrix composites are just now being developed for these demanding applications, and thus, the study of the durability of these materials is in its infancy (Courtright, 1991). The state of development of these candidate materials is reviewed in the following discussion.

Oxide-based ceramics have long been used as linings in containment vessels for hot materials (metals, glasses, cement, etc.) and hot gases, at temperatures often in excess of 1500°C (2732°F), because of their chemical compatibility with these hot materials and with the ambient processing conditions where metals and polymers simply cannot perform. However, their low thermal conductivities and generally high thermal expansion result in poor thermal-shock resistance. In addition, their creep resistance (resistance to permanent deformation under load) is generally inferior to materials such as nitrides and carbides. The nitrides and carbides also exhibit superior thermal-shock resistance compared with oxide-based ceramics.

Two classes of non-oxide structural ceramics—silicon carbide (SiC) and silicon nitride (SiN)—are emerging as candidate materials from which to fabricate components for use in heat-recovery equipment, heat engines, and high-temperature industrial equipment. Composites containing a silicon phase or molybdenum silicides are also available or are being developed for high-temperature components. These materials are all thermochemically unstable in air or oxidizing environments and owe their long life to the formation of a passivating silicon dioxide layer which has among the lowest permeabilities for oxygen of any oxide.

Matrix materials that are alumina-based are being considered primarily because of the availability of a novel processing technique in which an alumina-aluminum matrix can be "grown" through a fiber or particle preform by an oxidation process (Newkirk et al., 1986). Composites based in this technology may find application in less demanding components such as the engine exhaust nozzle.

The availability of high-temperature fibers has been reviewed by Tressler and DiCarlo (1993). In brief, the current polycrystalline oxide fibers have inadequate strength and creep resistance for structural applications above ~1000°C (1832°F). The single-crystal sapphire fiber with the crystal c-axis aligned along the fiber axis is extremely creep resistant, creeping only at temperatures greater than 1550–1600°C (2822–2912°F). This fiber is being developed in smaller diameters so that it may eventually be available in diameters of interest for ceramic-matrix composites. Other single-crystal or solidified eutectic oxides are also being researched, but their suitability and availability are yet to be established.

Polymer-derived, silicon-based fibers have been widely used in ceramic-matrix composite development because of their superior high-temperature strength compared with the oxide-based fibers and their handling characteristics. Nicalon® fiber is the most widely used. Nicalon contains nanocrystalline SiC and carbon grains and an amorphous Si-O-C phase. The creep resistance of the original Nicalon is inadequate for service in combustor and nozzle components. Recent work in Japan and France has resulted in a low-oxygen content fiber which is more creep resistant but still does not meet the goals for a 1300–1400°C (2370– 2550°F) structural application (Chollon et al., 1993; Hasegawa, 1993).

Development efforts are concentrating on fully crystalline SiC fibers fabricated either from polymer precursors or from an extruded powder preform which is then sintered. The combination of excellent creep resistance and high strength at elevated temperatures has not been achieved, but materials development efforts have shown sufficient promise that programs to develop composite fabrication methods are using Nicalon as a model fiber, assuming that an adequate polycrystalline SiC fiber will eventually be available.

The required feature of the mechanical response for a ceramic-matrix composite is "graceful" or noncatastrophic failure which implies crack deflection at the fiber-matrix interface. Thus, engineering an interface with a low-fracture energy relative to the matrix and the fibers is a critical issue in ceramic-matrix composite technology. For the composites now being tested for various applications, the interfacial zone or interphase is often carbon or graphite either deposited during fabrication (usually by chemical-vapor deposition) or exsolved from the fiber (in the case of Nicalon in glassceramic matrices). Although this type of interphase is being used in successful applications at high temperatures (e.g., rocket engine components, etc.) for SiC/SiC composites, it has been shown to be unacceptable for structural applications on oxidizing ambients where long lives are required (Jamet and Lamicq, 1993).

New materials for the fiber-matrix interphase region must be developed. Chemical-vapor-deposited boron nitride is being developed as an interphase material. Microporous, crushable oxides such as zirconia are being considered. The development of a stable, durable interphase material is critical for ceramic-matrix composite applications.

The SiC/SiC composite system is currently the most promising candidate for combustor applications. Chemical-vapor infiltration is the most advanced processing method, but the finished part is not fully dense. Melt infiltration and reaction (e.g., molten silicon reacting with carbon) is also being considered. The Silcomp® process (Luthra et al., 1993) was originally developed for monolithic, particle-reinforced, or discontinuous-fiber-reinforced, reaction-sintered SiC and is now being adapted for continuous-fiber ceramic composites.

4

Degradation Mechanisms

The properties of the aluminum alloys, titanium alloys, nickel-based superalloys, polymer-matrix composites, and ceramic-matrix composites that are candidate materials for HSCT (High-Speed Civil Transport) structures and engines may degrade with time at the elevated temperatures associated with the operation of the aircraft. The general degradation mechanisms (i.e., the physical event or chain of events that underlie observed degradation effects) that must be considered include:

- microstructural and compositional changes,
- time-dependent deformation and resultant damage accumulation,
- environmental attack and the accelerating effects of elevated temperature, and
- synergistic effects among the above.

The lack of prior service experience with the candidate materials makes the design of advanced high-speed vehicles dependent on predictive models to characterize long-term behavior. The development of such predictive models and their application with some level of confidence requires a thorough understanding of the degradation mechanisms of interest.

Deformation and failure mechanism maps can provide a framework for understanding the time-dependent damage (Ashby, 1983). Mechanisms of property degradation and damage accumulation under complex thermomechanical and environmental conditions, especially those uniquely associated with the operation of HSCT, are discussed in this chapter.

ALUMINUM ALLOYS

Historically, the chief damage mechanisms for aluminum alloys in aircraft applications are corrosion and fatigue, mechanisms generally associated with an aging fleet (Bucci and Konish, 1994). There is currently a great deal of work being supported by the Federal Aviation Administration, NASA, and the materials and aircraft industries to characterize the effects of corrosion and multiple site fatigue accumulation. Information is sparse concerning damage mechanisms associated with high-temperature applications of aluminum alloys. Potential damage mechanisms include microstructural changes, fatigue, creep, and environmental effects.

Elevated-temperature exposure under applied stress can introduce a number of microstructural changes, including nucleation and growth of new phases; formation of subgrains; changes in dislocation density, configuration, and distribution; and nucleation, growth, and coalescence of microcracks. Many of these changes will occur in the absence of stress, while others can be exacerbated by stress. Cyclic stresses may induce accelerated local overaging (coarsening) of the microstructure (Martin and Doherty, 1976), as well as promote the nucleation of microstructural damage (e.g., microcracks, voids, reinforcement fracture in composites) at various sites in the material. In monolithic materials, grain boundaries, inclusions, and other second phases and microstructural inhomogeneities may provide nucleation sites, while in metalmatrix composites, additional damage sites are provided by the presence of the reinforcement (Singh and Lewandowski, 1993a).

Determination of the most critical degradation mechanisms depends on what properties are important in a particular application. For example, if strength is critical, coarsening of the matrix precipitates during elevated-temperature service will be important; if toughness is critical, grain-boundary precipitation or the development of a precipitate-free zone will be important; and if creep or fatigue are critical, the nucleation, growth, and coalescence of microcracks will be important.

Microstructural Changes

Residual Stresses

The level of residual stresses in aluminum alloys and aluminum-matrix composites are strongly dependent on processing conditions, heat treatment, and thermal excursions. In monolithic aluminum alloys, changes in the processing conditions (e.g., hot and warm working, cold working, rolling, etc.) significantly affect the mechanically induced residual stresses, while quenching and heat treatment produce thermal residual stresses and the precipitation of second phases which possess lattice parameters different than that of the matrix. The mismatch in lattice parameters produces local residual stresses that may be reflected in the macroscopic mechanical properties. The level of residual stresses are affected by subsequent thermal exposures and prestraining.

In addition to the residual stresses produced via processing, heat treatment, and straining in the monolithic materials, the introduction of reinforcements with different coefficients of thermal expansion than the matrix alloy induces additional thermal residual stresses as well as the possibility of increased mechanical residual stresses because the reinforcements do not deform in a plastically deforming matrix (Bourke et al., 1993; Liu et al., 1993; Withers and Clyne, 1993). As with monolithic alloys, the levels of residual stress may be affected by subsequent thermal exposures and prestraining (Liu et al., 1993).

Strength

Coarsening of matrix precipitates is expected to be the major cause of the loss of yield strength in the 2XXX-series ingot alloys. In addition to many theoretical treatments of the effects of applied stress on precipitate growth and coarsening, there are experimental observations of particular relevance (Weatherly and Nicholson, 1968; Singer and Blum, 1977). For example, Singer and Blum (1977) looked at the effects of various thermomechanical processes on the creep behavior of 2618. They showed that the loss of precipitation strengthening during overaging was accelerated by the application of stress. The early work of Weatherly and Nicholson (1968) showed that aging with applied stress produced a significant acceleration in the rate of coarsening of precipitates in an Al-Cu-Mg system. Extended exposures at the intended service temperatures, even without stress, may degrade the yield strength of the ingot 2XXX alloys. Recent data show degradation of tensile yield strength of ingot 2XXX alloys in the T8-type tempers after 1,000 hours at 135°C (275°F; Angers, 1994). Experience on materials used in the Concorde showed a degradation in such properties in early-generation aluminum alloys tested prior to utilization on the Concorde (Peel, 1994). Coarsening of the dispersed phase in dispersionstrengthened alloys such as X8019 is not expected to be a problem at the temperatures of interest (see Figure 3-1).

Toughness

Various researchers have highlighted the importance of microstructural features on the degradation of toughness because of overaging in both monolithic and metal-matrix composite systems (Lewandowski et al., 1987, 1989; Lewandowski, 1989; Klimowicz and Vecchio, 1990; Manoharan and Lewandowski, 1990). In conventional aluminum alloys such as 2XXX-, 6XXX-, and 7XXX-series alloys, age hardening generally produces increases in strength and an accompanying decrease in fracture toughness, while overaging subsequently recovers the toughness while decreasing the strength (Garrett and Knott, 1978; Chen and Knott, 1981; Lewandowski and Knott, 1985). However, microstructural changes such as gain-boundary precipitation, the development of precipitate-free zones, and changes in the deformation modes have been shown to significantly affect the strength/toughness relationship primarily through a reduction in the fracture-critical properties (Vasudevan and Doherty, 1987). For example, the toughness is not recovered upon overaging in a variety of metal-matrix composites (Lewandowski et al., 1987, 1989; Lewandowski, 1989; Klimowicz and Vecchio, 1990; Manoharan and Lewandowski, 1990) and A1-Li alloys (Vasudevan and Doherty, 1987; Blankenship and Starke, 1991).

Deleterious effects of elevated-temperature exposure have been noted in experimental ingot 2XXX-series alloys aimed at high-speed aircraft applications. As shown in Figure 4-1 , some degradation in both strength and toughness were observed after 1,000 hours at 135°C (275°F). Creep deformation of 2618-T6 has been shown to degrade fracture toughness and increase the amount of intergranular fracture (Bobrow et al., 1991).

Time-Dependent Deformation and Damage Accumulation

Fatigue

Fatigue resistance is degraded by the nucleation, growth, and coalescence of voids or microcracks. The level of residual stresses discussed earlier can reduce the level of applied stresses that can be accommodated in service without the nucleation and growth of microcracks. High-cycle fatigue resistance is sensitive to the nucleation of microcracks at

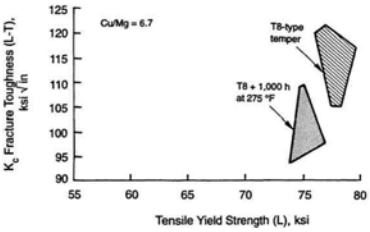


FIGURE4-1 Fracture toughness versus tensile yield strength for sheet from an experimental Al-Cu-Mg-Mn-Ag alloy in the T8-type temper and after 1,000 hours at 135°C (275°F). Source: Alcoa (1995).

microstructural inhomogeneities, while fatigue crack growth thresholds are affected by the level of residual stresses and crack tip shielding produced by variations in the microstructure. For example, in Al-Li alloys, microstructural features such as the planarity of slip deformation (Blankenship and Starke, 1991), as well as the presence of grain-boundary precipitates and precipitate-free zones (Vasudevan and Doherty, 1987), have been shown to affect the fatigue properties. In the threshold regime, the intense slip localization and the resulting crack tip bifurcation produces nonplanar fracture surfaces and reduces the local stress intensity for crack growth (Blankenship and Starke, 1991). It has been demonstrated that the reinforcements in metal-matrix composites improve high-cycle fatigue resistance while decreasing both the low-cycle fatigue resistance and fatigue crack growth resistance (Allison and Jones, 1993).

Creep

Although a great deal is known about the relationships between creep and microstructure, most authors have restricted their theoretical and experimental studies to secondary ("steady-state") creep. While there are no theoretical treatments that describe primary creep rates in terms of microstructural features, the effects of alloying, grain size, percent stretch, and extent of aging have been investigated for 2618 and other precipitation-strengthened aluminum alloys.

Creep resistance appears to improve with increasing grain size in precipitation-strengthened alloys. For example, the creep resistance of Hiduminium-RR58 (alloy 2618) improved progressively with increases in grain size (Doyle, 1969a, b). As shown in Figure 4-2 , the creep resistance of 2519-T87 at small strains improved with increases in grain size, in the range from 15 to 250 microns (Alcoa, 1995).

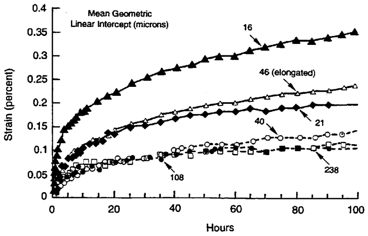


FIGURE 4-2 Creep strain versus time for 2519-T87 products having ing grain sizes, tested at 175°C (347°F) under an initial stress of 20 ksi. Source: Alcoa (1995).

The effect of existing strain (pre-strain) on subsequent creep is different in pure metals and alloys than in particlehardened materials. In pure metals and alloys, cold work improves the creep strength by removing part or all of the primary creep strain. The opposite trend has been observed in the precipitation-strengthened aluminum alloys. For example, Wilson (1973) and Peel (1994) showed that pre-strain in 2618 variants, either before or after artificial aging, has a deleterious effect on creep resistance. Doyle (1969a, b) also showed that while tensile properties of Hiduminium-RR58 were increased by cold work after quenching, the creep resistance was reduced. For microstructures that were composed of a fine precipitate and any of three types of dislocation substructure, such as a uniform dislocation distribution, a cellular distribution, or well-defined subgrains (e.g., in commercial and modified 2024, 7075, and 2618 and an Al-Cr alloy), creep strengths were decreased relative to a condition where only fine precipitates were present (Clauer and Wilcox, 1974).

A similar effect of pre-strain was observed in the dispersion-strengthened powder metallurgy Al-Fe-Ce alloys (Alcoa, 1995). Increasing rolling reductions tended to increase the rate and extent of primary creep, presumably because a nonequilibrium substructure was created. Reheats between rolling passes served to anneal the substructure and reduce primary creep rates.

In general, while applying creep deformation (pre-creeping) at the temperature and stress of interest may reduce the extent and rate of primary creep, pre-straining to large strains at different temperatures and strain rates may have the opposite effect. This may be particularly true in metal-matrix composites where it has been demonstrated that pre-straining produces damage (Liu and Lewandowski, 1988; Brechet et al., 1991; Lloyd, 1991; Singh and Lewandowski, 1993a), the extent of which is very dependent on the reinforcement size, matrix microstructure, and nature of the reinforcement-matrix interfaces (Singh and Lewandowski, 1993a).

Environmental Effects

Degradation mechanisms due to service environmental interactions that need to be considered for aluminum alloys include corrosion, stress corrosion cracking, hydrogen embrittlement, solid-metal embrittlement, and liquid-metal embrittlement. Susceptible sites within the material, such as grain-boundary regions, interfaces, and precipitates are favored sites for embrittlement by all of the above means. The microstructural features that affect the performance of various monolithic aluminum alloys in such environments were summarized by Holroyd (1989). Grain-boundary precipitation or precipitate-free zones are favored sites for corrosion due to the differences in composition and the resulting electrochemical behavior. A number of the other embrittlement mechanisms also depend on the matrix temper, making thermal exposure effects on the resulting microstructure relevant. Although very little published work exists on the behavior of metal-matrix composites under various environmental exposures, research indicates that susceptibility to corrosion, stress corrosion, and hydrogen embrittlement are extremely sensitive to the electrochemical behavior of the reinforcement and reinforcement-matrix interfaces, as well as to the microstructural features outlined above (Singh et al., 1992a, b).

Heavy-metal impurities, introduced through the use of recycled scrap containing lead or bismuth, may significantly accelerate the evolution of creep damage and sustained load cracking in aluminum alloys at temperatures ranging from −4–80°C (25–176°F). Sustained load cracking can occur at rates in excess of 100 mm/yr at high stress intensities in 6XXX-series alloys containing levels of lead or bismuth that are within the specification limits for those alloys (Lewandowski et al., 1987, 1992). Of concern to the long-term behavior of those systems is that crack initiation and growth near the threshold value of crack initiation is very dependent on time, temperature, and heavy-metal impurity level, as well as the distribution of the heavy-metal impurities in the microstructure. Such problems have been reported in the electric power industry overseas, the domestic automotive industry, and in the pressure vessel industry.

Summary: Aluminum Degradation Mechanisms

Potential damage mechanisms associated with high-temperature applications of aluminum alloys include microstructural changes, fatigue, creep, and environmental effects.

- Elevated-temperature exposure under applied stress can introduce a number of microstructural changes including coarsening of the matrix precipitates (important in strength-critical applications) and grain-boundary precipitation or the development of a precipitate-free zone (important in toughness-critical applications)
- Fatigue resistance is degraded by the nucleation, growth, and coalescence of voids or microcracks. High-cycle fatigue resistance is sensitive to the nucleation of microcracks at microstructural inhomogeneities, while fatigue crack growth thresholds are affected by the level of residual stresses and crack tip shielding produced by variations in microstructure.
- Creep resistance appears to improve with increasing grain size. Also, cold work reduces creep resistance in precipitation- and dispersion-strengthened aluminum alloys.
- Degradation mechanisms due to service environmental interactions that need to be considered for aluminum alloys include corrosion, stress corrosion cracking, hydrogen embrittlement, solid-metal embrittlement, and liquid-metal embrittlement.

TITANIUM ALLOYS

The primary results of degradation due to aging in titanium alloys in the temperature range of 200°C (392°F) or less would be possible loss of strength, fracture toughness, and fatigue crack growth resistance at these temperatures. Changes in microstructure (e.g., precipitation of chromium and iron intermetallic phases) during long-term exposure at the service temperature and their effect on these properties is of concern. Creep deformation and rupture at temperatures of 200°C (392°F) or less is not likely to be relevant. However, establishing the highest recommended use temperature for the selected alloys from the point of avoiding creep deformation and crack growth is a worthwhile goal and will help the designers of supersonic aircraft to assess safety margins and also to optimize the use of these alloys.

Three interrelated problems associated with the complexity of fracture processes in titanium alloys, and the possibility of time-temperature-hydrogen-dependent failure modes, could hinder development of high-strength and high-toughness titanium alloys for HSCT applications. These problems include the effects of microstructural variations on deformation and local fracture, uncertainties in intermediate temperature deformation behavior, and hydrogen embrittlement.

Microstructural Variations

Fundamental fracture relationships—particularly among microstructure, deformation mode, and local fracture resistance—are not sufficiently understood for beta titanium alloys. Because of the large number of different microstructures that can be developed by thermomechanical processing (e.g., variations in beta grain size, alpha volume fraction, grain-boundary alpha formation, alpha morphology on aging, and metastable phases), a better understanding of the relationship between processing conditions, resulting microstructure, and properties in this class of alloys, analogous to what has been developed for aluminum alloys, needs to be established. In addition, the effects of crystallographic texture on properties and property anisotropy need to be better understood.

For example, consider the relationships among tensile ductility, fracture toughness, and grain size. Ductility depends on grain size, and the strength/ductility balance can normally be improved by thermomechanical treatments that refine grain structure. Fracture toughness appears to be less sensitive to changes in grain size; consequently, the strength/toughness balance may be less affected by grain refinement (Kawabe and Muneki, 1993). Initiation and growth fracture toughness are expected to depend on tensile strength, ductility, and modulus. The relationships between basic mechanical properties and fracture toughness have been represented by strain-controlled micromechanical models (Gangloff, 1994). A detailed analysis of the strength/toughness balance must consider such relationships, including basic understanding of ductility-microstructure relationships, and must involve careful measurement of both initiation and growth fracture toughness. Grain-structure-dependent crack path tortuosity will affect crack growth resistance, but not plane-strain initiation toughness, if the latter is carefully measured.

Deformation Processes

Studies on deformation and fracture of titanium have focused on either near-ambient or relatively high temperatures. Little data are available concerning the effects of moderate service temperatures and loading rates on alloy behavior; the assumption is that ductility and toughness will increase with increasing temperature within the HSCT range. Concerns include the possibility for dynamic strain aging from solute such as oxygen or carbon to reduce tensile ductility and toughness by affecting microvoid growth and coalescence, the possibility for thermally activated slip localization in locally soft regions of the microstructure, time-temperature effects on hydrogen embrittlement, and deformation and fracture behavior at cryogenic temperatures.

Environmental Effects

The dissolved hydrogen content of HSCT-candidate titanium alloys could increase during processing, component fabrication, or elevated-temperature service in aggressive environments, such as airplane hydraulic fluid, and subsequently degrade tensile ductility and fracture toughness.

Although beta titanium alloys are believed to be tolerant of dissolved hydrogen (Eylon et al., 1994), additional study is required to verify their resistance to hydrogen effects. Brittle hydrides do not form in body-centered-cubic beta alloys due to exposure in hydrogen-producing environments such as modest pressure gases and electrolytes. The diffusivity of hydrogen in beta is relatively rapid (similar to that in high-strength martensitic steels), even at 25°C (77°F; Schutz, 1993). In contrast, the alpha phase is susceptible to both internal hydrogen embrittlement (IHE) and hydrogen environment embrittlement (HEE), as demonstrated by a variety of studies on alpha-beta alloys such as Ti-6Al-4V and Ti-6Al-6V-2Sn (Nelson, 1974; Lucas, 1990; Moody and Costa, 1991). Hydrogen is relatively insoluble in alpha, with a hydride phase possible, and is slow-diffusing compared with diffusion in beta (Schutz, 1993). Hydrogen effects are likely to be microstructure sensitive; either primary or precipitated alpha in the beta matrix may reduce hydrogen tolerance, particularly if this phase is arrayed in a continuous path along beta-grain boundaries or if this phase promotes locally intense slip.

HSCT-candidate alloys may be prone to hydrogen embrittlement. Such alloys are generally higher strength than the alpha-beta and beta titanium alloys that have been examined to date; high strength exacerbates hydrogen embrittlement (Gangloff, 1988). Based on results for alpha-beta alloys with lower concentrations of beta-stabilizing elements, Ti-6-22-22 could be prone to hydrogen embrittlement. Metastable beta alloys such as Beta-21S, Ti-15-3, and Beta-C are embrittled by predissolved hydrogen during subsequent, relatively rapid-rate loading at 25°C (77°F; Young and Scully, 1993, 1994). The fracture strain of both peak-aged and lower-strength solution-treated alloys was degraded by dissolved hydrogen. Intergranular and a variety of transgranular cleavage and slip-band cracking modes were promoted by hydrogen, without evidence for hydriding of either the alpha phase or the continuous beta matrix. Several factors exacerbated IHE, including higher hydrogen concentrations (between 100 and 1,000 ppm by weight), triaxial constraint, as well as grain-boundary alpha colonies or locally intense planar slip. IHE and HEE susceptibility is likely coupled (Nelson, 1974). Peak-aged Beta-21S and Beta-C are susceptible to intergranular environmental crack propagation in aqueous chloride (or chloride stress corrosion cracking) when subjected to actively rising stress intensity levels at about one-half of the planestrain fracture toughness (Grandle et al., 1994; Young et al., 1995). This behavior mirrors the well-known brittle cracking of alpha-beta alloys such as Ti-6Al-4V and parallels the IHE behavior (Nelson, 1974).

High-strength or high-toughness HSCT-candidate titanium alloys may be prone to HEE in typical aircraft environments. Low-cost beta and Beta-CEZ alloys have not been examined to assess their susceptibility to hydrogen embrittlement, including the effects of temperature, loading rate, and the effects of moderate hydrogen concentration. The HEE resistances of low-cost beta, Beta-CEZ, and Ti-6-22-22 are not characterized. While most IHE and HEE studies emphasize brittle cracking under plane-strain conditions, the range of HSCT component geometries dictates consideration of adverse hydrogen effects on both plane-strain and plane-stress deformation and fracture processes.

Summary: Titanium Degradation Mechanisms

Three primary factors need to be considered in long-term, elevated-temperature applications of high-strength and high-toughness titanium alloys for HSCT applications, including:

- the effect of microstructural variations (e.g., variations in beta grain size, alpha volume fraction, grain-boundary alpha formation, alpha morphology on aging, and metastable phases) should be developed, analogous to what has been developed for aluminum alloys,

- the effects of moderate service temperatures and loading rates on alloy behavior, including the possibility for dynamic strain aging, thermally activated slip localization, time-temperature effects on hydrogen embrittlement, and deformation and fracture behavior at cryogenic temperatures, and
- the degradation of tensile ductility and fracture toughness due to dissolved hydrogen from aggressive environments such as airplane hydraulic fluid.

SUPERALLOYS

The degradation mechanisms that affect nickel-based superalloys include overaging of microstructure, fatigue, creep, and oxidation. The trade-off that needs to be made among the competing properties is difficult, as whatever is done to improve one property usually affects all of the other properties. An example of this is shown in Figure 4-3 , in which several key properties are shown to vary with one of the controllable parameters in the microstructure grain size. There are many controllable parameters such as grain size, microstructure, and concentration of major and minor alloying elements that can be optimized to yield the balance of properties.

Microstructural Changes

Overaging of the superalloy microstructure depends on time, temperature, and stress. All of the nickel-based superalloys used in gas turbine engines are metastable under use conditions. Characterization of selected alloys must be performed to define the safe-use limits of the alloy for the engine-operating environment. Creep experiments are the primary mechanical characterization test to determine the limits for an alloy.

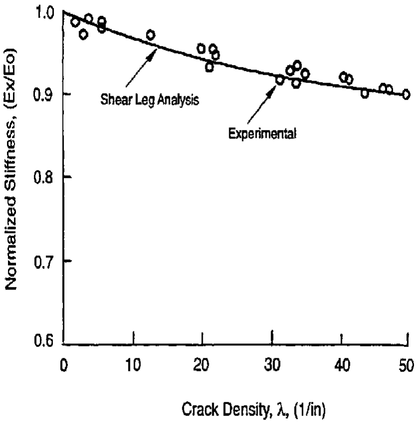


FIGURE 4-3 Effect of grain size on a variety of mechanical properties for nickel-based superalloys.

The strength of nickel alloys is derived primarily from the ` ′ particles that precipitate in the alloys on cooling. These particles are generally ordered arrays of Ni3A1, although cobalt can substitute for nickel and niobium, and titanium and tantalum can substitute for aluminum (the general chemistry of these particles is given as [Ni, Co]3[Al, Ti, Nb, Ta]). The alloys undergo heat treatment to obtain a uniform array of particles of a specific size and spacing to achieve the maximum strength and stability. However, at high temperatures and stresses the larger particles grow while the smaller ones dissolve—a process known as Ostwald Ripening—which in time change both the structure and behavior of the grains. This process can be slowed by altering the balance of elements that form ` ′ particles and adding large atoms that diffuse slowly in the matrix, slowing down the entire coarsening process. The problem with this approach is that new flat and brittle phases, called topologically close-packed (TCP) phases, can form and cause strength reduction at grain boundaries. A primary goal of most alloy development is to avoid the formation of TCP and to develop as stable a microstructure as possible with the many constraints imposed on the process.

Deformation and Damage Accumulation

Superalloys develop damage from cyclic applications of stress and strain. The most prevalent sources of mechanical damage are low-cycle fatigue and creep deformation. Both processes are at work in most turbine applications.

Creep failure is generally not a problem in turbine or compressor disks, but creep deformation can be a tremendous problem. As the disk creeps during operation it can redistribute stresses, allowing accelerated fatigue in other locations. Also, creep deformation of an engine disk can cause compressor or turbine blades to rub against the outer case. The allowable creep in a turbine disk is very small, generally less than 0.2 percent creep in the life of the disk. Creep, in conjunction with stress and oxygen effects at the tip of a crack, can result in dramatic accelerations in crack growth rates. This is referred to as dwell crack growth, creep crack growth, or time-dependent crack growth.

Oxidation

Oxidation in nickel-based alloys or structural castings is more than simple surface oxidation, which in many ways would be an easier problem to solve. Since the oxidation rates for grain boundaries are far greater than the rate for bulk oxidation, grain boundaries usually serve as sites for oxidative degradation.

Over the years the reduction or elimination of grain boundaries via directional solidification and single-crystal processing has greatly extended reliability of blade alloys. However, single-crystal and directionally solidified alloys are high in cost, have directional properties, and exhibit a large reduction in low-temperature strength and fatigue properties compared with conventional alloys.

Another approach to improve oxidation resistance is to include alloying additions that inhibit the embrittling effects of oxidation on the boundaries to the basic alloy chemistry of elements. The alloying elements that have the greatest effect are those that partition primarily to the grain boundaries, including boron, carbon, hafnium, and zirconium. These elements are generally added in very small quantities, but assuming that they partition solely to the grain boundaries, they may be the primary elements locally at the boundary. The challenge in reducing grain-boundary oxidation is to add just enough of the correct alloying elements to inhibit oxidation while maintaining mechanical properties.

POLYMER-MATRIX COMPOSITES

Despite the myriad of composite materials and structural arrangements, there are a limited number of mechanical degradation mechanisms (NRC, 1991). These include:

- matrix cracking,
- delamination,
- fiber-bundle rapture,
- local compressive instability, and
- interfacial failure.

Any one of these damage modes may be small as regards the representative volume element of the structure in question and therefore viewed as subcritical. However, the combined effects of several damage modes may radically alter this picture. The complex coupling of any number of these damage modes is poorly understood. Furthermore, the entire process will be strongly influenced both by material types and structural lay-up.

For elevated-temperature applications such as the HSCT, the effects of various environmental factors must also be accounted for in addition to the mechanical degradation modes. Continuing damage accumulation is induced and driven by combined cyclic loads, high-temperature exposure, oxidative attack, solvent infusion, moisture, and other factors. The coupling process linking the growth of various damage modes and the external environmental drivers will undoubtedly prove complex.

Damage mechanisms to consider for elevated-temperature composite applications include thermal oxidation, hygrothermal (combined moisture and temperature) effects, matrix cracking, and microstructural changes. The evaluation of the degradation of polymer-matrix composites is complex, requiring not only an integration of many contributing factors, but also an assessment of poorly understood synergistic accelerations in damage accumulation as driven by external factors. Moisture absorption, high-temperature exposure, heating (and cooling) rates, and loading rates represent a number of those factors that affect basic composite properties such as toughness, glass transition temperature, and strength. The combined influence of such factors on the failure mechanism may be pivotal in deriving any reliable modeling process.

Microstructural Changes

High-temperature thermosetting polymers such as bismaleimides commonly incorporate discrete toughening phases, typically 25–35-weight percent of a soluble thermoplastic polyimide in granular or particulate form, to improve impact resistance. Isothermal air aging studies at temperatures above 150°C (302°F) have shown a tendency for these systems to undergo phase separation that is clearly distinguishable under examination in the scanning electron microscope. Using a common optical microscope, distinct color differences can be seen between the two phases, with both phases showing considerable darkening as exposure time increases. This phase separation progresses from the surface to the interior and is assumed to be driven by differences in oxidation rates of both the bismaleimide and the added toughening agent. Phase separation has a deleterious effect not only on matrix toughness, but can also lead to matrix cracking since phase boundaries represent discontinuities with associated stress concentrations. This combined degradation phenomenon can be seen generally after 5,000 hours of exposure and represents a valid concern for long-term HSCT applications.

Damage Accumulation: Matrix Cracking

Perhaps the most critical damage mechanism operating in high-temperature polymeric composites is the formation of transverse ply cracks (shown schematically in Figure 4-4) and in-plane microcracks in matrix polymers of multiaxial composites. Matrix cracking can result from initial laminate processing, mechanical static, and fatigue loading (Reifsnider and Giacco, 1990), residual stresses resulting from hygrothermal exposures, thermal cycling, and combined effects of mechanical and environmental cycles (Sensmeier, 1994). As the cycles (mechanical or thermal) advance, matrix cracks become more pronounced and increase in density until a saturation level is reached (NRC, 1991).

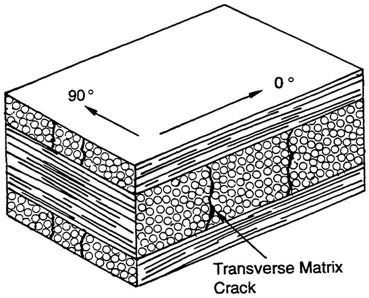


FIGURE 4-4 Schematic of transverse matrix cracks in a cross-plied composite laminate.

Fiber anisotropy [1] and differences between thermal expansion coefficients of the matrix and fiber can result in residual thermal stresses during processing or exposure to temperature. These stresses can cause fiber-matrix interfacial failure or radial cracking (in the matrix radiating from fiber surfaces).

The fundamental cause of thermally induced transverse matrix cracking in a laminate is the residual stresses resulting from differences in thermal expansion of the lamina in longitudinal (parallel to the fiber orientation) and transverse (perpendicular to fiber orientation) directions ($\alpha L \neq \alpha T$). Hygrothermal (combined moisture and temperature) cycling of composite laminates can produce transverse matrix cracks that initiate in surface plies and progress deeper into the laminate with accumulating cycles. The rate and severity of transverse matrix cracking is dependent on several conditions, including matrix properties, fiber properties (especially thermal expansion and stiffness), processing conditions, service conditions (including temperature cycle and humidity), ply thickness, and ply stacking sequence.

Composite strength, stiffness, and thermal properties as well as failure modes can be affected by transverse matrix cracking. Figure 4-5 shows a reduction in stiffness as a function of crack density for a cross-plied carbon/epoxy laminate. Glass/epoxy cross-plied and pseudoisotropic laminates made from nonwoven unidirectional fabric and laminates made from 181-style cloth had stiffness reductions of 15–20 percent due to microcracking caused by subjecting the laminates to cyclic tension loading (McGarry and Wilner, 1968).

In addition to damage-induced reduction of matrix-dominated mechanical properties, the advancing microcracking promoted higher uptake of moisture deeper in the laminate (Carey, 1957; Anderson and Healey, 1958; Epstein and Bandaruk, 1964).

Environmental Effects

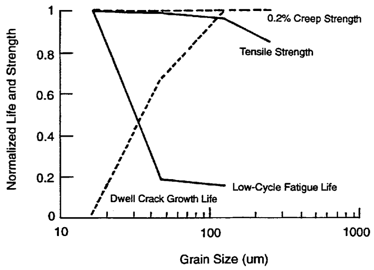
Thermal Degradation and Oxidation

Exposure to high temperatures can cause chemical degradation of composite-matrix polymers. Thermal degradation usually implies chemical reactions associated with polymer chain scission as a result of temperature or diffusion of small molecules (e.g., O2). Degradation of composite-matrix polymers will more likely be due to thermal instability and the accelerating effects of oxidative attack.

Polymer degradation in an inert atmosphere is the result of the breaking of covalent bonds in the polymer network. The result is a reduction in molecular weight and eventually volatilization of low-molecular-weight fragments (void growth). This process is important and is used positively in the production of polymer-precursor carbon and ceramic materials. The susceptibility of a polymer to thermal degradation is a function of the bond strength (Rodriguez, 1970). The thermal stability of high-performance polymers in an inert atmosphere are generally very good due to their highly crosslinked and aromatic nature.

Unfortunately, most high-temperature aircraft applications involve exposure in oxidizing environments (e.g., ambient air). While both carbon fibers and matrix polymers are susceptible to oxidative degradation, the degradation of the fibers is negligible at the service temperatures envisioned for application of polymeric composites (Magendie et al., 1990). However, oxidation of high-temperature matrix

FIGURE 4-5 Normalized axial modulus of [0, 902]s carbon/epoxy laminate as a function of transverse crack density. Source: Lee and Daniel (1990).



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[1] Coefficients of thermal expansion of fibers (such as carbon or polymeric fibers) are different in the longitudinal and transverse directions.

polymers must be considered in composite design and characterization.

HSCT-candidate systems have exhibited varied susceptibility to oxidation (Brunner, 1994). Matrix systems that have been evaluated include polyimides (Bowles et al., 1993), bismaleimides (Stenzenberger et al., 1976; Magendie et al., 1990), cyanate esters, benzocyclobutene, and thermoplastics such as polyarylenes (Arnold and Maskell, 1991). Oxidation is usually characterized in terms of weight loss. In general the candidate materials can be ranked in terms of oxidation resistance from most stable to least stable: polyimides ≈ polyarylenes ≫ bismaleimides ≈ cyanate esters ≫ epoxies (Hipp et al., 1993).

Microstructural studies have shown that oxidation of high-temperature polymers is largely a surface phenomena (Nam and Seferis, 1992). Oxidation reactions in the interior relies on mass-transport processes, including diffusion of oxygen inward and subsequent diffusion of reaction products outward.

In carbon-reinforced composites, oxidation of matrix polymers is strongly influenced by geometry and ply orientation. Matrix oxidation is dominated by the exposed surface and the fiber-matrix interface, progressing inward from exposed edges along the fiber direction as shown in Figure 4-6. The nature of the fiber-matrix interphase region and the influence of fiber coatings or sizings are critical in limiting oxidation of the composite. The presence of significant matrix cracking makes more surface available and can greatly accelerate oxidative degradation throughout the laminate.

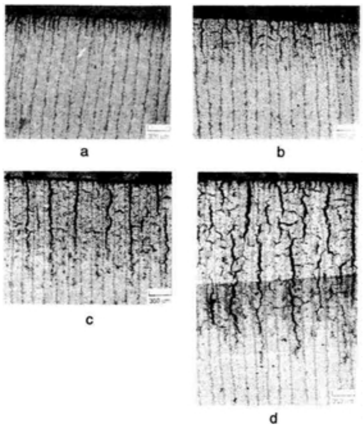

FIGURE 4-6 Progression of oxidative degradation zone in a carbon/bismaleimide composite. Aging conditions are (a) 28, (b) 70, (c) 164, and (d) 262 hours at 290°C (554°F). Source: Nam and Seferis (1992). Reprinted by permission of the Society for the Advancement of Material and Process Engineering.

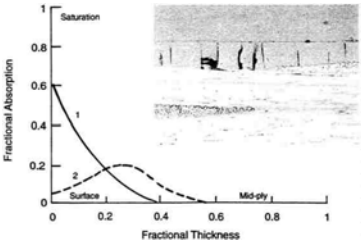

FIGURE 4-7 Schematic of composite laminate moisture profile and micrograph of surface-matrix cracking: (1) initial moisture load; (2) moisture profile after hygrothermal cycles.

Composite mechanical properties, especially interlaminar and interfacial shear, and flexural have been shown to be seriously degraded due to oxidative damage (Bowles, 1993; Hipp et al., 1993). Much more work needs to be done to understand threshold damage conditions and the effects of low levels of oxidation on composite performance.

Hygrothermal Effects

The detrimental effects of moisture, particularly at high temperature, are often underestimated. Since the projected flight cycle for the HSCT reaches hot, dry conditions during the supersonic cruise phase of each flight, many believe that HSCT applications can be considered to be dry structure for evaluation purposes. However, although the time to moisture saturation is long, all structures will carry a moisture load when entering flight. On a global basis the moisture level may be low, but the surface plies could carry significant moisture levels. Concentration gradients (Figure 4-7)—from high moisture levels at the surface to near dryness at the midplies—along with subsequent desorption in the near-surface plies and redistribution of moisture during flight can lead to significant residual stresses or outer-ply delamination or blistering during rapid heating. The effects of moisture are dependent on many factors, including thickness, material type, prevailing humidity, flight temperature profile, time and conditions between flight times, and presence of matrix cracking. Potential long-term hygrothermal effects include microvoid generation and reduction in intrinsic mechanical properties due to matrix plasticization. Potential short-term hygrothermal effects include matrix cracking, outer-ply delamination, or surface blistering during rapid heating.

Although it is well known that moisture plasticizes matrix polymers, with an apparent increase in toughness, studies have shown that repeated cyclic exposures designed to simulate flight histories can result in growing microcracking initiated at the surface as shown in the micrograph in Figure 4-7. Moisture has been shown to increase the residual stresses that can lead to matrix cracking in many systems, including carbon/polyimide, carbon/bismaleimide, and aramid/epoxy. As described in previous sections, matrix cracking can increase the composite's vulnerability to other damage accumulation mechanisms, including fatigue loading, chemical attack by fluids, and changes in mechanical or chemical properties of the matrix or interface. McGarry and Wilner (1968) showed that for cross-plied glass/epoxy laminates the weight gain resulting from one day water immersion increased significantly as a result of microcracking caused by tension fatigue (50–75 percent weight gain increase for 30 percent cyclic stress and 100–150 percent weight gain increase for 50 percent cyclic stress).

Simple hygrothermal cycling, with no externally applied loads, has been shown to cause a multiplicity of damage mechanisms for composites including (1) alteration or loss of intrinsic properties, (2) microcracking, (3) microvoid generation, (4) delamination, and (5) surface blistering.

For example, hygrothermal exposure of thermoplastic polyimide resins—AFR700B and Avimid®N—intended for very high-temperature service (up to 371°C [700°F]) leads to significant loss in glass transition temperature (T_g) (>50°C [90°F]). Contrary to previous expectations, neither matrix system offers a stable T_g nor 371°C (700°F) performance capability. Adopting a strict adherence to MIL-HDBK-17B standards, the safe material-operating limit would be less than 260°C (500°F) in spite of the fact that the initial, dry T_g was greater than 400°C (752°F). As the wet T_g decreases, approaching the upper exposure cycle temperature, the elevated internal moisture vapor pressures can be sufficient to generate both interior microvoids and small surface blistering.

Amorphous, high-temperature thermoplastic polyimides, such as Avimid N and AFR700B, that are subjected to a post-cure thermal treatment to attain very high T_g are glassy polymers in an energy state above thermodynamic equilibrium. The basic, intrinsic properties of both resins can change significantly under hygrothermal exposures. Exposures at temperatures well below the dry T_g results in a cumulative, permanent reduction in T_g. Matrix-dominant mechanical properties (e.g., shear modulus, compressive strength, and transverse tensile strength) that are closely coupled to the T_g, particularly at elevated temperatures, can be significantly affected (Cornelia, 1994). High-temperature humidity exposures effectively plasticize the matrix, accelerating polymer relaxation processes toward thermodynamic equilibrium. As the T_g decreases, the acceptable upper limit of the service temperature also decreases. Under similar conditions another thermoplastic polyimide, Avimid K3B, shows no alteration of intrinsic properties. Although bismaleimide systems have not exhibited this behavior, highly crosslinked systems were not totally immune; the polyimide PMR-15 shows significant loss of T_g (20–25°C [36–45°F]) after a modest number of hygrothermal cycles. Morphological and crystalline character have a strong influence on matrix-dominant properties. The effects of hygrothermal exposures on matrix morphology must be considered when determining acceptable performance.

Summary: Polymer-Matrix Composite Degradation Mechanisms

Damage mechanisms to consider for elevated-temperature composite applications include thermal oxidation, hygrothermal (combined moisture and temperature) effects, matrix cracking, and microstructural changes.

High-temperature thermosetting polymers commonly incorporate discrete toughening phases to improve impact resistance. These systems can undergo phase separation that has a deleterious effect, not only matrix toughness, but it can also lead to matrix cracking.

Perhaps the most critical damage mechanism operating in high-temperature polymeric composites is the formation of transverse ply cracks and in-plane microcracks within the matrix of multiaxial composites. Matrix cracking can result from initial laminate processing, mechanical static and fatigue loading, residual stresses resulting from hygrothermal exposures, thermal cycling, and combined effects of mechanical and environmental cycles. Strength, stiffness, and thermal properties as well as failure modes are affected by the mechanical and chemical degradation of composites (Greszczuk, 1988). Generally, stiffness, strength, and coefficients of thermal expansion decrease with increases in microcrack density.

Exposure to high temperatures can cause chemical degradation of composite-matrix polymers. Degradation of composite-matrix polymers are generally due to thermal instability and the accelerating effects of oxidative attack. In carbon-reinforced composites, oxidation of matrix polymers is strongly influenced by geometry and ply orientation.

Hygrothermal effects can lead to significant residual stresses, outer-ply delamination, or blistering during rapid heating. The effects of moisture are dependent on many factors including thickness, material type, prevailing humidity, flight temperature profile, time and conditions between flight times, and presence of matrix cracking. Absorbed moisture can increase the residual stresses and lead to matrix cracking, whereas microcracking can accelerate moisture absorption and desorption.

CERAMIC-MATRIX COMPOSITES

Since the candidate ceramic-matrix composite materials are just now being developed, there is very little direct information about their durability. Therefore, the durability of the constituent materials is considered here to identify potential degradation mechanisms for these composites. This section includes a review of the degradation of the monolithic materials, a discussion of the degradation of the high-temperature fibers, and a discussion of the interphase (material at the matrix-fiber interface) durability.

Thermochemical Degradation

Recent reviews have summarized the high-temperature stability of non-oxide structural ceramics (Jacobson, 1993; Tressler, 1993). The review by Jacobson concentrated on the corrosive degradation of silicon-based (i.e., monolithic silicon carbide [SiC] and silicon nitride [SiN]) ceramics in combustion environments. Figure 4-8 shows the major types of corrosive attack as a function of reciprocal temperature. The passive region refers to the formation of a protective SiO_2 film that grows by diffusion of oxidants through the growing scale. Active oxidation refers to material removal by the formation of gaseous SiO (g). Reaction of the SiO_2 with the substrate to form volatile SiO(g) only occurs at the very highest temperatures. Molten salt deposition (e.g., $Na_2SO_{4)}$ can occur at lower temperatures and accelerate the passive oxidation by dissolving the SiO_2 film, leading to rapid rates of material removal and often to selective pitting of the substrate (Fox et al., 1990). Aerodynamic conditions can affect these rates if the corrosive product is swept off the surface into the gas stream, leaving a fresh, reactive surface or a very thin protective film.

Current research suggests three major areas of concern with silica films:

- Influence of impurities (Zheng et al., 1992; Opila, 1994). It appears that small amounts of such elements as sodium and aluminum accelerate the growth rate of silica by an order of magnitude or more.
- Ease of reduction of SiO_2 to SiO(g). The formation of SiO(g) via a classical, active oxidation mechanism only occurs under extreme conditions. However, there are many situations where both oxidizing and reducing gases are present (e.g., fuel-rich combustion in the HSCT). Under these conditions, SiO_2 can form on a silicon-based component, but it is readily reduced to SiO(g). Recent work at NASA Lewis has demonstrated this both in furnace and burner tests (Opila et al., 1994; Opila and Jacobson, in press).
- Formation of silicon hydroxy species. It is well known that in steam atmospheres SiO_2 readily hydrates to form Si $(OH)_4$(g) and $Si_2O(OH)_6$(g) (Brady, 1953; Kashimoto, 1992). High-pressure combustion environments contain substantial amounts of water vapor, and this volatilization has recently been observed at NASA Lewis in combustion atmospheres (Opila et al., 1994).

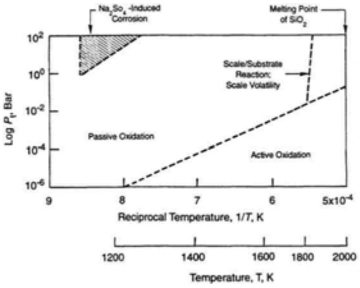

FIGURE 4-8 Major types of corrosive attack and degradation as an approximate function of reciprocal temperature ($P_{total} = P_{oxidant}$). Source: Jacobson (1993). Reprinted by permission of the American Ceramic Society.

These three issues have major implications in the application of SiO_2-protected materials to the HSCT. Only limited data are available to delineate the extent of each phenomena.

Because of the above effects, as well as the susceptibility of silica to basic molten salt attack, there has been an effort by several groups to develop refractory oxide coatings for silicon-based ceramics (Lee et al., 1994, 1995). These systems show the promise of combining the desirable physical and mechanical properties of a silicon-based system with the better durability of a refractory oxide. Mullite coatings on SiC show improved corrosion resistance. However, mullite contains silica at a fairly high activity. Recent developmental work suggests it may be possible to go from mullite to an even more refractory coating.

Non-oxide fibers are also subject to the same thermochemical degradative processes if they are exposed to the environment. In addition, the polymer-derived fibers undergo microstructural changes at elevated temperature which lead to altered mechanical properties (Bodet et al., 1993). Specifically, in the Nicalon fiber the Si-O-C phase decomposes to yield additional SiC particles and SiC grain growth with CO being a gaseous decomposition product. Encapsulation in an impermeable matrix or exposure at high temperature in a CO ambient suppresses this behavior, but in general the fiber degrades under long-term exposure.

The most critical chemical durability issue involves the interphase material. The carbon interphase can be actively gasified in an oxidizing ambient atmosphere, leaving ultimately a SiC/SiC interface that is too strong. Under the highest temperature conditions the interphase channel can fill with SiO_2 so that the removal of the interphase is limited to the near-surface region (Filipuzzi and Naslain, 1994). In service, the matrix will be cracked, providing points of interphase degradation.

The most common fiber coatings—carbon and boron nitride—are currently unacceptable because of their susceptibility to oxidation. The need for alternate fiber coatings is the major issue in the development of fiber-reinforced ceramicmatrix composites in their present form. Many efforts have been directed to this end, but the requirements of fiber pull-out (to provide toughness) and inertness with silicon (which is one of the most reactive elements) limit the possibilities. The issue of a microstructurally stable fiber is being pursued with the development of fully crystalline SiC fibers.

Mechanical Degradation: Effects of Corrosive Reactions

In addition to the purely thermodynamic and kinetic aspects of the corrosion reactions, a recognition is emerging that the selective attack of certain microstructural features can lead to nucleation of strength-limiting flaws. The time-dependent properties of slow crack growth and creep leading to creep damage are altered because of grain-boundary effects caused by reactions with the environment. Examples are the effects of oxidation in the high-temperature creep and fracture of βSi_3N_4 ceramics and the effects of oxidation on crack growth in sintered SiC. For temperatures below 1300–1400°C (2372–2552°F), crack growth is the key issue in non-oxide ceramics, particularly sintered and chemical-vapor-deposited SiC that are extremely creep resistant.

The primary parameter of concern for long-term reliability is the threshold stress intensity, K_{th}, above which crack growth will occur. Very short lifetimes of tens of hours are predicted from crack growth rate (V) versus stress intensity factor (*K*) data for components stressed above the threshold *K* value. Thus, environmental effects on the threshold *K* value are of critical importance in engineering design. For sintered α-SiC with boron and carbon-sintering additives, either preoxidation or testing in air caused a substantial reduction in the estimated value of K_{th} at 1200°C (2192°F) and 1400°C (2552°F; Minford and Tressler, 1983; Minford et al., 1983). In general, oxidation has a deleterious effect on crack growth in SiC materials. Recent studies of the effects of interphase oxidation and embrittlement of SiC/SiC composites with a carbon interface (e.g., Filipuzzi and Naslain, 1994) suggest that a carbon interphase is simply not going to be acceptable for long-lived composites.

Fibers that exhibit excessive creep or undergo slow crack growth can also be life limiting as observed for monolithic SiC (Tressler and DiCarlo, 1993). Rugg and Tressler (n.d.) have demonstrated the effect of crack growth in the stressrupture behavior of a developmental sintered SiC fiber. The limiting aspect of the c-axis sapphire fibers as load-bearing members is slow crack growth which leads to unacceptable stress-rupture characteristics above ~ 1000°C (1832°F; Newcomb and Tressler, 1993).

Thus, although the phenomena that lead to degradation of the individual constituents of current ceramic-matrix composites are beginning to be understood, the study of the durability of any given composite system is just now beginning. Accelerated aging evaluations can be based only on degradation mechanisms for the constituent materials, not a detailed understanding of a composite system.

Summary: Ceramic-Matrix Composite Degradation Mechanisms

Based on the durability of the constituent materials, the most important degradation mechanism for ceramic-matrix composites for HSCT applications is thermochemical degradation (including corrosion and oxidation reactions) in combustion environments. The selective attack of certain microstructural features of the composite can lead to the initiation of flaws that affect slow crack growth and creep deformation processes.

RECOMMENDATION

The development and application of aging characterization tests and predictive models require a thorough understanding of the important basic materials properties and degradation and damage accumulation mechanisms to provide confidence in their ability to accurately assess service life. Also, an understanding of the damage mechanisms and affected mechanical properties can provide important criteria for the developers of high temperature materials so that material candidates can be improved. The evaluation of basic materials properties and definition of critical degradation mechanisms for these materials is, at present, incomplete. The scarcity of available property data makes the analysis of subsequent test results to determine aging responses challenging.

- The committee recommends that NASA emphasize fundamental work to characterize materials properties and, most important, to determine critical degradation and damage accumulation mechanisms over a broad range of environmental conditions. This work should allow determination of the mechanisms that are likely to have the greatest influence on component durability.

5

Accelerated Methods for Characterization of Aging Response

When the fundamental materials properties have been defined and the important damage mechanisms have been established, the response of materials to service conditions can be determined. The characterization of aging responses in structural materials entails establishing the fundamental relationships between service and environmental exposure and structure and property metrics. To be useful in analytical models, the relationship between exposure and material structure or property must include degradation rates; dependence on environmental factors such as temperature, pressure, loads, or concentrations; and the effect on a significant performance metric.

Much work has been done to evaluate fundamental materials aging responses for the isolated damage mechanisms identified in chapter 4. Much of this work is described in this chapter for specific materials. However, the potential of synergistic effects between mechanisms is not completely understood. This chapter describes characterization methods to evaluate the aging responses in HSCT- (High-Speed Civil Transport) candidate materials. Current methods are explored, and data needs and gaps are identified for metals, polymeric composites, and ceramic-matrix composites.

The long service-life requirements of HSCTs and the limited time available for development, evaluation, and validation of material candidates makes accelerated aging characterization necessary. Methods include accelerated testing and accelerated aging. *Accelerated testing* is required for mechanisms that involve progressive accumulation of damage or deformation that could lead directly to failure. For accelerated test methods it is important to develop equivalence between test progression and service exposure time or flight cycles. *Accelerated exposures* are used to produce end-of-life microstructure or damage states for subsequent characterization tests. For accelerated aging, the calibration of test progression with service exposures is not as critical as the confidence that the microstructural features produced using accelerated exposures represents end-of-life conditions. In some cases, both accelerated aging and accelerated aging methods are required.

METALLIC ALLOYS

The accelerated aging and test methodologies and approaches for monolithic metallic systems (aluminum alloys, superalloys, and titanium alloys) have considerable similarities. The load, stress, and stress-intensity parameter levels; the thermal profiles and test temperatures; and the test environment vary among the variety of alloy systems and applications. However, the testing and data analysis procedures have considerable similarities which are attributable to commonality in the durability concerns for HSCT structure and engine components. The primary durability concerns include:

- brittle and ductile fracture,
- mechanical- and thermal-fatigue crack initiation and growth,
- variable amplitude loading including dwell periods,
- creep and creep-fatigue crack initiation and growth,
- environment-assisted crack growth, and
- long-term microstructural stability under exposure to stress and temperature.

The linear elastic and elastic-plastic fracture mechanics approaches for predicting brittle and ductile fracture, respectively, are well established and are not discussed in this report. Similarly, the approaches for predicting classical fatigue crack growth behavior under rapid cyclic loading are also very well established.

The focus of this section is on methods for characterizing time-dependent degradation mechanisms which include microstructural degradation, creep, and environmental and creepfatigue degradation of materials. Table 5-1 and Table 5-2 show the degradation and deformation mechanisms discussed in chapter 4 and the approaches one might take in characterizing materials response. In each case, the most important variables, mechanistic models, empirical models, and ways to accelerate the test are presented. The characterization models and techniques are generally effective in describing the progression of particular degradation processes. More work is required to determine the synergistic effects between degradation processes and to relate test exposures to the service environment.

The Concorde Experience

Much can be learned from the Concorde experience, which may be relevant to new high-speed transports. There are numerous references to the Concorde's structural development (Harpur, 1968; Strang and McKinlay, 1978), to the selection of materials for that aircraft (Doyle, 1969a, b; Murphy, 1972), and to long-term data on those materials (Spuhler et al., 1963; Martinod et al., 1969; Webb, 1977; Butt and Wilson, 1980; Butt, 1985).

TABLE 5-1 Critical Degradation Mechanisms for Advanced Metallic Alloys

Damage Mechanism	Properties Most Affected	Most Important Variables	Mechanistic Models	Empirical Models	Ways to Accelerate Test
Precipitate coarsening	Strength Toughness	Applied stress Exposure temperature Exposure time	Coarsening models [a] Strengthening model [b]	Arrhenius analyses Avrami analyses	Increase temperature and/or stress
Grain boundary precipitation and precipitate-free zone formation	Toughness Corrosion	Applied stress Exposure temperature Exposure time		Arrhenius analyses Avrami analyses	Increase temperature and/or stress
Grain growth and secondary recrystallization	Toughness Corrosion Creep	Applied stress Exposure temperature Exposure time	Grain growth models [c]	Arrhenius analyses Avrami analyses	Increase temperature and/or stress
Changes in dislocation structure	Creep Fatigue	Applied stress Exposure temperature Exposure time	Dislocation models [d]	Arrhenius analyses Avrami analyses	Increase temperature and/or stress
Void formation and cracking	Toughness Creep crack growth Fatigue	Applied stress Exposure temperature Exposure time	Void formation models [e]	Arrhenius analyses Avrami analyses	Increase temperature and/or stress

Sources:

[a] Lifshitz and Slyozov (1961), Wagner (1961), Speight (1968), Ardell (1972), Shiflet et al. (1979), Davies et al. (1980).
[b] Brown and Ham (1971), McElroy and Szkopiak (1972), Gerold (1979), Martin (1980).
[c] Cahn (1983).
[d] Bendersky et al. (1985).
[e] Nix and Gibeling (1983).

The aluminum alloy selected for the primary structure of the Concorde (CM001) has a nominal composition of Al-2.5Cu-1.5Mg-0.22Si-1.1Fe-1.1Ni (Harpur, 1968; Strang and McKinlay, 1978). This material is a specially processed clad sheet of the alloy known in the United Kingdom as RR58 and in France as AU2GN. It was selected over other candidates such as 2024-T81, 7075-T6, and L73 (a British equivalent of alloy 2014) because of its static strength, fatigue strength, and especially because of its creep strength. To evaluate the structural alloy, static strength data were acquired at room temperature and elevated temperatures for materials exposed for 20,000 hours at estimated cruise temperatures. Fatigue was evaluated by testing at 120°C (248°F) with a constant mean stress of about 25 percent of the ultimate strength. Creep strength was defined as the stress for which creep strains would be limited to less than 0.1 percent for a given time. Creep data were acquired at 120°C (248°F) under a steady stress of 177 MPa (25.6 ksi). [1]

There are a number of earlier studies that summarize the results from long-time tensile and creep tests on Concordecandidate alloys (Spuhler et al., 1963; Martinod et al., 1969; Webb, 1977; Findley and Lai, 1978; Butt and Wilson, 1980; Butt, 1985). A review of such prior work may not provide the engineering data needed for HSCT design, but should provide insight, test procedures, and models that could be useful for HSCT materials.

Creep Deformation and Failure

Creep failure has been avoided in high-temperature structures in power plants by choosing maximum service temperatures and maximum allowable stresses to restrict creep deformation to less than 1.0 percent strain in 100,000 hours. In the 20,000 hours of service experience with the Concorde, creep failures have been successfully avoided (Peel, 1994) by use of simple design rules and well-accepted approaches for predicting creep behavior. Figure 5-1 shows the relationship between applied stress and creep test duration to achieve a 0.1 percent creep strain for various high-temperature aluminum alloys demonstrating the superiority of alloy 2618 over other alloys. Extrapolation of the creep data was accomplished by the well-established Larsen–Miller (Larsen and Miller, 1952)

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[1] This concept was very different than the concept used by engine designers, where creep-rupture times were of greater importance.

and Dorn–Sherby (Dorn and Starr, 1954) parameters. Deformation and failure mechanism maps (Frost, 1985) have been developed since the design of the Concorde. The purpose of the deformation mechanism maps is to ensure that the proper deformation mechanisms are accounted for in predicting material responses under conditions other than those tested. An example of the transient deformation mechanism maps for 316 stainless steel is shown in Figure 5-2. Such maps can be developed for the candidate aluminum and titanium alloys that will serve as guidelines for selecting the allowable stress and temperature ranges to ensure edequate creep resistance.

TABLE 5-2 Critical Deformation Mechanisms for Advanced Metallic Alloys

Deformation Mechanism	Most Important Variables	Mechanistic Models	Empirical Models	Ways to Accelerate Test
Creep	Operating stress Operating temperature Operation time	Creep deformation models [a]	Larson–Miller (and modifications such as Manson–Haferd, Orr–Sherby–Dorn, Manson–Brown) [d]; projection [e]; minimum commitment method [d]	Increase temperature and/or stres
Thermal fatigue	Temperature range Number of cycles Frequency	Linear cumulative damage analysis [b]	see [f]	Increase temperature range
Mechanical fatigue	Operating stress range Operating temperature Number of cycles Frequency	Linear cumulative damage analysis [c]	see [f]	Increase temperature and/or stress range and/or frequency

Sources:

[a] Ashby (1972), Lagneborg (1972).
[b] Imig (1976), Kiddle et al. (1976).
[c] Imig and Garrett (1973), Imig (1976).
[d] Manson and Ensign (1979).
[e] Evans et al. (1990), Wilshire and Evans (1994).
[f] Imig and Garrett (1973), Imig (1976), Kiddie et al. (1976).

Creep-Fatigue Failure

Creep-fatigue failures caused by mechanical loading as well as thermomechanical fatigue are a concern in the design of HSCT structures and engines. The materials are likely to experience an increased risk for such failures if adequate consideration to these failure modes is not given during the design. The jet engine and the electric power generation industries have experienced such concerns in the past in the design of their components and therefore have experience in designing against creep-fatigue failures. This problem is new, however, to the aircraft structure design. Creep-fatigue failures have not been encountered in the Concorde service (Peel, 1994). However, due to the more severe service conditions expected for the HSCT, thermomechanical fatigue with

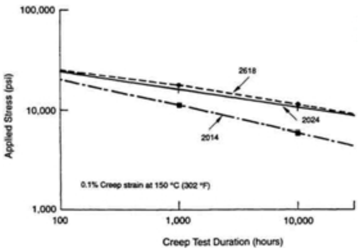

FIGURE 5-1 Relative creep strength of candidate alloys for the Concorde. Source: Peel (1994). © British Crown Copyright 1994, Defence Evaluation and Research Agency. Reproduced with the permission of the Controller, Her Majesty's Stationery Office.

possible contributions from creep could be a significant concern.

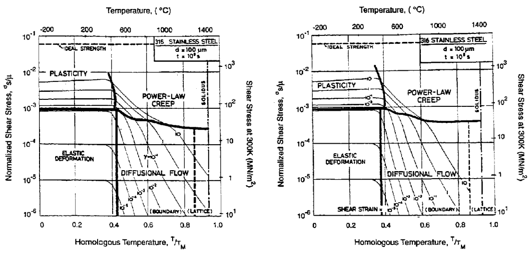

FIGURE 5-2 Deformation mechanism maps for 316 stainless steel after exposure for (a) 3 years and (b) 30 years. Note: Strains were calculated from constitutive equations. Source: Frost (1985).

Creep and Creep-Fatigue Crack Growth

Since damage-tolerant analysis is standard for all civil aircraft structures and is also built into certification procedures (Kan, 1994), it is important to explore the available fracture mechanics approaches and test procedures for predicting creep and creep-fatigue crack growth in structures. Time-dependent fracture mechanics concepts have been well developed for creep-ductile metals (Saxena, 1991), including the development of a recent American Society for Testing and Materials (ASTM) standard for creep crack growth testing (ASTM, 1994). Figure 5-3 shows creep crack growth rate for Cr-Mo steels used in power plant components. Similar studies have also been performed on titanium alloys (Dogan et al., 1992) and aluminum alloys (Lang et al., 1991; Hamilton and Saxena, 1994). Current data and techniques are insufficient to develop well-accepted creep crack growth approaches to creep-brittle materials such as the high-temperature aluminum alloys and titanium alloys.

Creep-fatigue crack growth rates for trapezoidal waveforms have been characterized by the average value of the C_t parameter as shown in Figure 5-4 for a variety of hold times ranging from 10 seconds to 24 hours and also including creep crack growth rate data. Although such nice consolidation of creep-fatigue data for several hold times into a single trend cannot be expected for all materials, the approach itself of correlating creep-fatigue crack growth rates to a global crack tip parameter is widely used.

Standard ASTM test procedures are available for conducting creep crack growth testing. The current standard does not

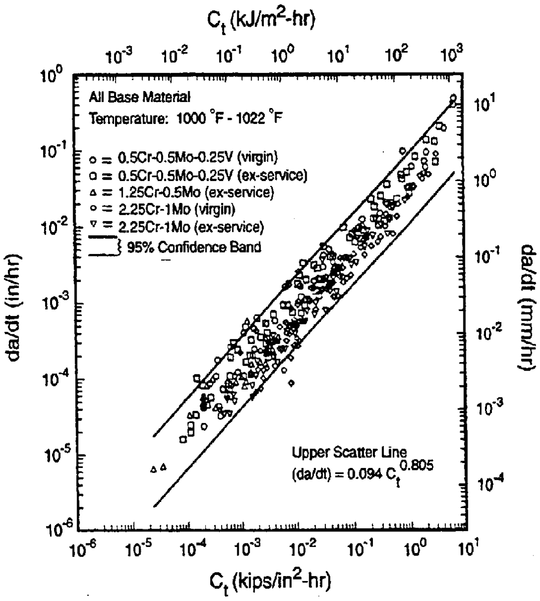

FIGURE 5-3 Creep crack growth behavior of Cr-Mo and Cr-Mo-V base materials. Note: The plot includes all ex-service and new material data. Reprinted from Saxena et al. (1988), with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

apply to creep-brittle materials which include many of the HSCT-candidate materials. However, the subcommittee E.08.06 of ASTM is currently actively working on extending this method to the creep-brittle materials. No standard test procedures are available for conducting creep-fatigue crack growth testing, however, it is a subject of active research.

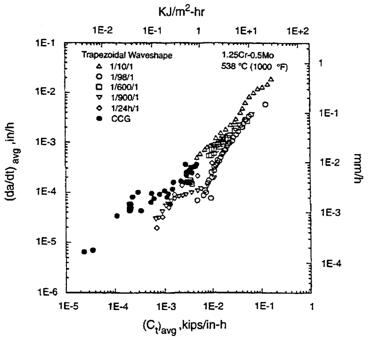

FIGURE 5-4 Comparison between creep crack growth and creep-fatigue crack growth data in terms of Ct Source Yoon et al. (1993) Reprinted with permission of Kluwer Academic Publishers

The creep and creep-fatigue crack growth tests require from a few weeks to one year to complete. In tests that last one year, it is possible to obtain crack growth rate information at growth rates as low as 10^{-5} in./h (1.3×10^{-3} mm/h). These data are in the range useful for design and also for setting realistic inspection intervals. For example, if the flaw tolerance of an aircraft structure that is inspected every 10,000 hours is 0.25 inch (6.35 mm) and the crack size that can escape detection during inspection is 0.05 inch (1.27 mm), the maximum allowable average crack growth rate can be $0.45/10{,}000 = 4.5 \times 10^{-5}$ in./h (1.14×10^{-3} mm/h). The measured crack growth rate data is below the above rate. Hence, there is no need for data extrapolation in this case.

Acceleration and Analytical Methods

Microstructural Changes

The mechanistic models referenced in Table 5-1 for deformation mechanisms and microstructural changes can be applied effectively to predict aging responses for single mechanisms. The synergistic interactions that are encountered when multiple, possibly competing, mechanisms are present add significant complexity to aging analysis. Current mechanistic models do not provide accurate predictions under these conditions.

It may be beneficial to use a more empirical approach to aging characterization when degradation mechanisms cannot be evaluated separately. For example, although techniques exist to describe the rate of overaging using a model for precipitate coarsening, the actual overaging process may involve a number of simultaneous processes (e.g., coarsening of one type of precipitate, the dissolution of another, the formation of grain-boundary precipitates, and the development of precipitate-free zones), and, typically, the models for these processes are not particularly well developed. Attempts at summing all of the relevant processes would likely result in very questionable results, making an empirical treatment more appealing.

An Alcoa study used a simple Arrhenius analysis (as described in the following text box and Figure 5-5) to determine the activation energy for overaging (Alcoa, 1995). The result of this analysis could be considered to be an “effective” activation energy for overaging, which would include all of the ongoing processes. To determine the activation energy for overaging, plots of room-temperature tensile yield strength after exposure versus exposure time were used. An example of these data is shown in Figure 5-6. The data from this figure were used to produce the plots of ln 1/t versus 1/T in Figure 5-7. Note that this analysis was carried out using four different

RATE EXPRESSIONS—ARRHENIUS ANALYSIS

A simple relationship that underlies many of the empirical and semiempirical degradation rate relationships described in this chapter is the Arrhenius rate equation. The Arrhenius relationship expresses the rate constant (k) as:

$k = A \exp(-Q/RT)$.

Assuming that the activation energy (Q) and pre-exponential factor A are constant and independent of temperature, the relationship above can be expressed as:

$\ln (t/t_{ref}) = Q/R[(1/T)-(1/T_{ref})]$,

where t and T are time and temperature, respectively. The activation energy can be determined from the slope of ln t versus 1/T at an equivalent property time (Salin et al., 1992), as shown in Figure 5-5. Arrhenius analysis can be applied to a range of rate relationships. For instance, this type of analysis has been applied in the characterization of a number of aging characteristics including secondary (“steady-state”) creep (Dorn and Starr 1954; Angers, 1991), overaging of aluminum alloys (Angers, 1991), and weight loss due to thermal degradation or oxidation (Salin et al., 1992).

values for the overaging stress; the parallel lines indicate that the value for the activation energy is independent of stress, at least over the range examined.

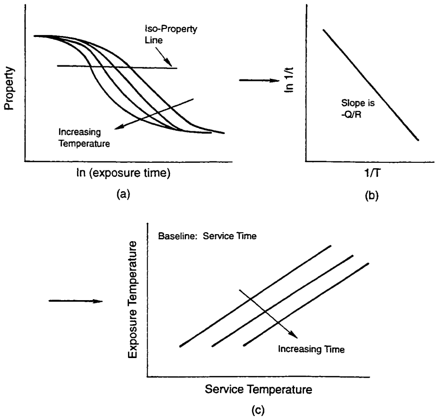

FIGURE 5-5 Schematic showing use of the Arrhenius expression for describing a reaction or property degradation rate. Source: Alcoa (1995).

Accelerating Creep Tests

There are several empirical and analytical methods for accelerating a test, most focusing on accelerating creep tests (Manson and Ensign, 1979). The Larson–Miller parameter, for example, is an empirical method generally used to predict creep-rupture times or steady-state creep rates at temperatures higher than the service temperature. The Goldhoff–Sherby, Orr–Sherby–Dorn, and Manson–Halford analyses are modifications to the Larson–Miller method and were developed to provide better fits to experimental data. Unfortunately, preliminary analyses on 0.1 percent creep and creep-rupture data from 2XXX-series aluminum alloys suggest that none of these empirical methods are particularly applicable for use with these materials (Alcoa, 1995).

A number of studies addressed the acceleration of creep tests at the time that the Concorde was being developed or used data generated during that time (Harfert, 1970; Imig and

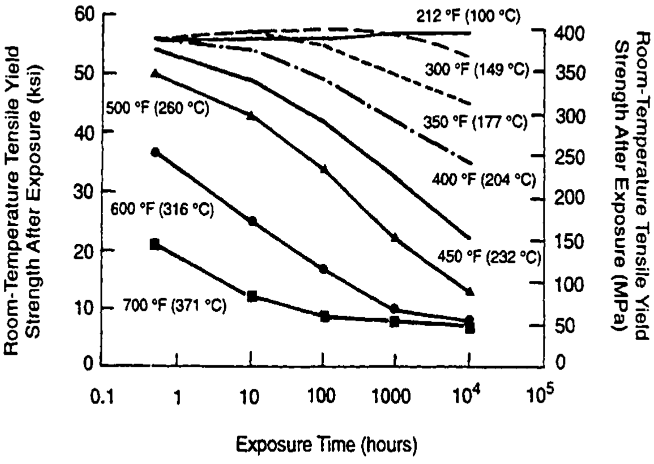

FIGURE 5-6 Room-temperature tensile yield strength as a function of exposure time at various temperatures for 2618-T651 extrusions. Source: Alcoa (1995).

Garrett, 1973; Imig, 1976; Kiddie et al., 1976; Findley and Lai, 1978; Cho and Findley, 1984; Wilshire and Evans, 1994; Evans et al., 1990). Findley and Lai (1978) and Cho and Findley (1984), for example, developed a viscous-viscoelastic model with a replacement of a temperature-compensated time for actual time, using tension and torsion data for alloy 2618-T61 in the range of temperatures of 200°C (392°F) to 230°C (446°F). Harfert (1970) studied two titanium alloys and alloy 2024-T3 and found that differences in creep temperatures and stresses caused different types of damage, even when the strain was held constant.

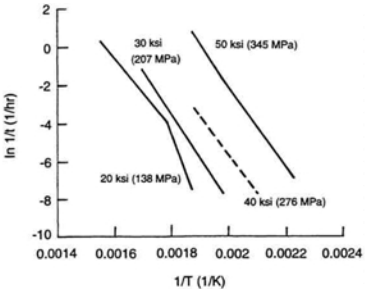

FIGURE 5-7 Plot of ln (1/t) versus 1/T for 2618-T651 extrusions overaged to 50, 40, 30, and 20 ksi. Source: Alcoa (1995).

One study that achieved promising results and appears directly relevant to the current problem was carried out by Wilshire and Evans (1994). They used the projection concept to predict long-term creep-rupture properties for 2124-T851 from the results of constant stress creep curves. In this method, strain versus time data are fit to an equation involving four constants: 1, 2, 3, and 4. These constants have fundamental significance, as 1 and 2 describe the decaying primary strain component, and 3 and 4 describe the accelerating tertiary creep component. The key to the concept is that the log values vary linearly with stress. Hence, if one determines the four values for using shorttime tests at high stresses, the long-time values for , and hence, the long-time curves, can be predicted by extrapolation. By analyzing data from tests lasting 1,000 hours, rupture behavior in excess of 20,000 hours was successfully predicted. Additional work is needed to verify that the projection concept could be used to predict the times to produce small creep strains.

Very little work has been published on extrapolating results from high-temperature to lower-temperature tests, specifically in aluminum. Claeys and Jones (1984) attempted to accelerate a creep test of 6061-T6 by accelerating an elevated-temperature exposure. They used overaging data and creep-rupture data to determine the activation energies for the overaging and creep processes. Using this activation energy, they could then relate a long-time, low-temperature exposure to a shorter time at a higher temperature. Samples were then exposed at the higher temperature and then creep tested into the steady-state regime at the lower temperature. A pseudocreep curve was produced by placing line segments, having the slope represented by the steady-state creep rates, onto a creep strain versus time plot at the appropriate position with respect to the time axis (i.e., at times adjusted using activation energy). While this method provided curves that satisfactorily reproduced real long-time test data, it has several drawbacks. The accelerated exposures did not include an applied stress, suggesting that the match between pseudocreep curves and real creep curves was fortuitous. Also, the method does not provide any information about when sampies subjected to the service conditions might enter the tertiary creep regime or fail. Nonetheless, this novel approach warrants further consideration and may be able to be modified to predict behavior in the primary creep regime.

A large body of tensile and creep data from ingot metallurgy 2XXX aluminum alloys (including 2014, 2024, 2090, 2124, 2219, 2519, and 2618) was analyzed at Alcoa using the Arrhenius analysis (Alcoa, 1995). Specifically, creep stresses for different levels of creep strain were of interest. For some alloys, there were data for several tempers and product forms, while for others data were limited. In many instances data were available for creep tests up to 10,000 hours. Plots of the stresses to reach 0.1 percent creep, 0.5 percent creep, and creep rupture were used to determine the activation energy for creep deformation. Examples of these data sets for 2618-T651 extrusions are presented in Figure 5-8. Figure 5-9 shows plots of inverse time versus inverse

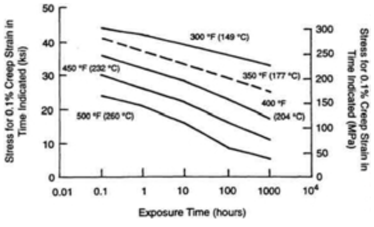

FIGURE 5-8 Stress for 0.1 percent creep strain as a function of time at various temperatures for 2618-T651 extrusions. Source: Alcoa (1995).

temperature used to determine activation energies for 0.1 percent and 0.5 percent creep at 207 MPa (30 ksi). The roughly parallel lines indicate that the activation energy for creep does not vary over a wide range of strain and is similar to the activation energy for overaging.

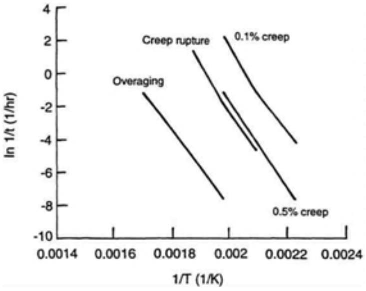

FIGURE 5-9 Plot of ln (1/t) versus 1/T for 2618-T651 extrusions overaged to 30 ksi, crept to 0.1 percent, 0.5 percent, or rupture. Source: Alcoa (1995).

Other work on heavy-metal impurity embrittlement of aluminum alloys has successfully used both single-specimen and multiple-specimen fracture mechanics tests to determine crack growth rates over a range of test temperatures in order to determine an activation energy for crack growth (Lewandowski et al., 1992). This has been successfully used to estimate crack growth rates at different test temperatures. In addition, crack linkage in the near-threshold regime is particularly important for the continued growth of the crack. There may be considerable specimen-to-specimen variations in the crack initiation and growth behavior due to differences in the microstructure, level of impurities present, and the distribution of the heavy-metal impurities. The effects of systematic changes in these parameters on the subsequent threshold and crack growth behavior have been successfully modeled using Monte Carlo simulations (Singh et al., 1992a, b). These simulations were patterned after those successfully used in predicting the behavior of stress corrosion cracks of pipeline steels where it is known that failure is caused by the coalescence of a multitude of individual microcracks (Singh and Parkins, 1990; Singh, 1991). Such modeling enables multiple simulations to run in order to provide information on the probabilistic aspects of crack initiation and growth as well as the effects of extrapolating data from single-specimen tests to multiple specimens. The use of such models in combination with single-specimen tests has been successful in predicting lifetimes of structures in service that contain cracks of various sizes. Other experimental and theoretical treatments of creep crack growth include studies by Fu (1980), Sadanda and Shahinian (1981), Bensussan et al. (1984), and Nikbin et al. (1986).

Accelerating Fatigue Tests

Imig and Garrett (1973) and Imig (1976) investigated the possibilities for reducing fatigue test time for supersonictransport materials and structures in tests of Ti-8Al- 1Mo- 1V and Ti-6Al-4V with simulated Mach 3.0 flight-by-flight loading. The effects of design mean stress, the stress range for ground-air-ground cycles, the simulated thermal stress, the number of stress cycles per flight, and salt corrosion were included in their studies. They conducted accelerated tests (2 seconds per flight) and real-time tests (96 minutes per flight), used a linear cumulative damage analysis, and concluded that they were successful in that the fatigue lives were generally within a factor of two of the lives from real-time tests.

Kiddle et al. (1976) conducted a study of thermal fatigue in box beams of CM001 under mechanical and thermal stresses. They showed that they could accelerate thermal-fatigue tests very predictably by a factor of two by increasing the thermal stresses through increases in the range of temperatures applied to the aircraft.

POLYMER-MATRIX COMPOSITES

Current Methods

Moderate- Temperature Applications

The methodology for substantiating the service life of polymeric-matrix composites for lower-temperature aerospace applications has been developed over the past 25 years (Whitehead et al., 1985; Vosteen and Hadcock, 1994). This work formed the basis for the requirements of MIL-HNBK17 (DOD, 1994). MIL-HNBK-17 provides guidance on the selection, design, and analysis of composite structures based on static ultimate strength considerations and the effects of three primary degradation mechanisms—impact damage, mechanical fatigue, and humidity (or fluid) exposure.

The substantiating approach for each of these mechanisms has been incorporated into the design verification process with evaluations on scales from coupon-level to full-scale structural components. This approach has been successfully developed to help offset the design analysis limitations in terms of predicting interlaminar stresses, damage initiation, and delamination growth. The final step of this approach is typically a full-scale component fatigue test on an impact-damaged structure. The acceleration of the primary damage mechanisms is achieved as described in the following sections.

Impact Damage. The structure is impacted prior to the fatigue test, substantiating both barely visible impact damage requirement for the life of the structure and the inspection interval required for visible impact damage. This is considered a conservative approach since the impact damage is done prior to fatigue cycling.

Mechanical Fatigue. The acceleration of fatigue testing in fiber-dominated constructions has been achieved by assessment of typical flight cycles. This approach, detailed by Jeans et al. (1980), determines how fatigue cycles are combined and what cycles can be truncated because low stress levels are well below fatigue thresholds. The balance of the cycles are typically conducted with higher loading to account for material data scatter, since typically only one article is tested. Fatigue is not generally a significant damage mechanism in fiber-dominated composite structures that meet impact-damage tolerance requirements. Components that experience significant interlaminar or out-of-plane loading can be susceptible to fatigue damage.

Humidity and Fluid Exposure. The methodology for accelerating humidity and fluid exposure tests are described in MIL-HNBK-17 (DOD, 1994). The accepted approach is to increase the temperature exposure to increase the diffusion rate. Design properties based on coupon tests are typically generated in a fully saturated humidity condition (85 percent relative humidity).

Real-time tests, using both flight service components and ground exposures, have verified the approach taken in first-generation composite applications. For example, NASA has conducted flight service evaluations of 350 components with over 5.3 million total flight hours and a large 10-year ground exposure program (Dexter and Baker, 1994).

High-Temperature Applications

Higher-temperature carbon/polyimide composites have been successfully certified for military airframe and engine applications (e.g., the carbon/PMR- 15 structures on the Navy F18 C/D and Air Force B-2 airplanes). The substantiation test methodology has been very similar to the process described above for lower-temperature applications except that a different criterion is used to determine the upper-use temperature for a material system. Carbon/epoxy systems have typically followed the approach where the material operating limit is considered to 28°C (50°F) below the glass transition temperature under moisture-saturated conditions (Whitehead et al., 1986). This generally keeps the material-use temperature low enough that irreversible resin morphology changes, thermal degradation and oxidation effects, and vapor-induced blistering are not a concern.

The moisture-saturated glass transition temperature is just one of the indicators of a high-temperature polymers upperuse temperature. The other indicators are resistance to transverse matrix cracking and to thermal degradation and oxidation. For the short-life, high-temperature military applications described above, these damage mechanisms are assessed by simulating the application environment in a real-time experiment. In contrast, little data are available on thermal and environmental degradation of high-temperature thermoplastic composites.

Accelerated Methods

For applications such as the HSCT where complex, long-duration exposures are expected, it would be economically and technically difficult to use a purely experimental test approach. Accelerated test methods and durability modeling will be required to predict end-of-life properties for these applications. The challenge will be to carefully augment the current composite verification approach with accelerated testing without overlooking critical damage mechanisms.

There are additional degradation mechanisms for high-temperature applications compared with the degradation mechanisms already discussed for lower-temperature systems. These degradation mechanisms include thermal and oxidative degradation, transverse matrix cracking, and hygrothermal (moisture plus temperature) effects. These degradation mechanisms are discussed in chapter 4. Table 5-3 shows critical degradation mechanisms for high-temperature applications of polymeric composites, the most important influencing variables, modeling approaches, and accelerated methods.

Thermal Degradation and Oxidation

Fundamental modeling of thermal degradation processes for high-performance polymers and composites is currently not available. A promising technique that may be applicable is computer simulation of molecular dynamics. These techniques have been applied to simulate the combustion of polyolefins (Nyden and Brown, 1993), however it is unclear whether these techniques could be accurately applied to high-performance polymers or composites.

The characterization of thermal degradation of a polymeric composite, under both oxidizing and inert conditions, is based on weight-loss measurements as a function of time and temperature. Characterization of weight-loss kinetics can be accomplished using thermogravimetric analysis (TGA) techniques. TGA characterization methods have been developed to determine the initial degradation of composites used in the manufacture of carbon/carbon composites (Nam et al., 1989) and for the degradation of HSCT-candidate materials (Grayson and Fry, 1994). These methods have been applied to both thermoplastic- and thermoset-matrix composites, and a generalized methodology to describe degradation kinetics of polymeric composites accounting for the anisotropy of composite degradation and for changes in the dominant degradation mechanism has been developed (Nam and Seferis, 1992; Salin et al., 1992).

TABLE 5-3 Critical Degradation Mechanisms for Polymeric Composites

Degradation Mechanism	Most Important Variables	Modeling Approach	Ways to Accelerate Tests	Missing Information
Matrix cracking	Processing parameters Temperature cycle range Static and fatigue loading Moisture/thermal cycle Number of cycles Ply thickness Residual stresses	Damage accumulation models [a]	Increase temperature cycle range Increase applied stress Increase	Effects of moisture Rate effects
Thermal degradation and oxidation	Temperature Oxygen concentration Exposure time Mass-transfer models	Reaction kinetics models [b]	Increase temperature Increase oxygen concentration	Chemical degradation models Effect of matrix cracking
Hygrothermal degradation	Exposure temperature Moisture concentration Heating rate	Moisture diffusion models [c]	Increase exposure temperature Increase moisture content Cycle moisture sorption	Effect of moisture on residual stresses Desorption effects Moisture gradient effects Effect of Matrix cracking Effect of imposed stress
Phase separation/ microstructural changes	Exposure time Exposure temperature Moisture content	none	Increase temperature Increase moisture content	Microstructural characterization methods Solubility models

Sources:

[a] Reifsnider and Highsmith (1981), Allen and Lee (1990), Nairn and Hu (1992).

[b] Nam and Seferis (1992), Salin et al. (1992).

[c] Shen and Springer (1976), Paplham et al. (1994).

In any evaluation of thermal degradation or oxidation of polymers, it is important to define the dominant degradation reaction and the changes in dominant reactions with temperature. This can be accomplished by analyzing the chemical make-up of the evolved gases using methods such as gas chromatography/mass spectroscopy or by analyzing the degraded polymer using methods such as diffuse reflectance Fourier-transform infrared spectroscopy.

While the initial degradation kinetics of the effects of edges and ply orientation can be evaluated using the methods above, the correlation of weight loss with mechanical performance is unsatisfactory. Current methods and previous evaluations have relied on exposure of test coupons or larger panels to isothermal or cyclic conditions (Kerr and Haskins, 1987; Pride et al., 1968). Weight loss is measured and specimens are machined and tested. Unfortunately, these tests do not necessarily account for the directionality of degradation reactions or on the preferred degradation at edges and at the fiber-matrix interface, nor do they take the presence of matrix cracking, component geometry, and coatings into account. Hence, measured property degradation is not sensitive to the level of degradation, and test results are not easily reproduced. The synergistic effects of time, pressure, and atmosphere on composite degradation can be established following the approach employed by Pride et al. (1968). Typical results are shown in Figure 5-10 and are for composites made with 181-style glass cloth and polyimide resin. The results shown in Figure 5-10 have been compressed into the single curve shown in Figure 5-11 by plotting the strength as a function of the Larson–Miller parameter, TR (C + log t), in which TR is the exposure temperature in degrees Rankine (Larson and Miller, 1952). Other properties, including elevated temperature properties, can be presented in a similar manner.

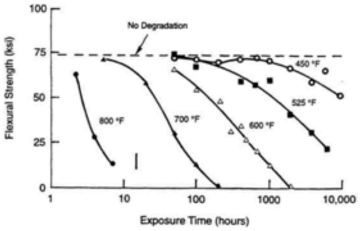

FIGURE 5-10 Variation of room-temperature flexural strength with exposure time at elevated temperatures. Source: Pride et al. (1968). Copyright (1968) SPI Composites Institute. Reprinted with permission.

Matrix Cracking

Transverse matrix cracking or in-plane microcracking can be thermally, hygrothermally, or mechanically induced. Current micromechanical and fracture mechanics models to predict matrix cracking susceptibility focus on mechanically (Reifsnider and Highsmith, 1981) and thermally (Bowles, 1984) induced matrix cracking. Matrix cracking can be characterized in terms of a saturation crack density, called the characteristic damage state that depends on ply properties, ply thickness, and stacking sequence (Reifsnider and Highsmith, 1981). The characteristic damage state has been shown to be independent of load history, initial stress, and environmental effects (except as they affect ply properties; Reifsnider and Giacco, 1990).

While the characteristic damage state provides a definition of an end-of-life condition, the development of matrix cracking and the threshold damage conditions are more difficult to model. Typically, these conditions have been identified by cyclic thermal or hygrothermal exposure testing (Brunner, 1994; Sensmeier, 1994), with test acceleration gained by rapid cycling, increased temperature range, or increased ply thickness (multiple adjacent plies of one orientation). The result would be a damage progression plot as shown in Figure 5-12. The results of this empirical approach are difficult to apply to conditions different from those tested. These tests have proven to be useful in screening or ranking materials, but have not enabled predictive capabilities.

Models that could be used to predict the onset and development of matrix cracking based on constituent properties must account for the dependence on processing conditions, residual stresses, thermal cycle range, and the effects of moisture content and distribution on the stresses that lead to cracking. A mechanistic model approach to predict the development of matrix cracking caused by both mechanical and thermal stresses has been developed (Nairn and Hu, 1992). Mechanistic modeling allows results to be applied over a broad range of conditions. The applicability of this type of modeling must be verified.

There are a number of analytical methods to determine stiffness reductions in a composite laminate because of matrix cracking (Allen and Lee, 1990). These methods include a shear-lag model (Highsmith et al., 1981; Highsmith and Reifsnider, 1982; Lim and Hong, 1989), self-consistent scheme (Laws et al., 1983; Dvorak, 1985), strain energy method (Aboudi, 1987), complementary strain energy method (Hashin, 1985, 1987), and the internal state variable approach (Allen and Lee, 1990). Additional work needs to be accomplished to allow the predicted ply properties developed in the theoretical models to be used to predict critical design properties of laminate or components, including thermal properties such as coefficients of thermal expansion, thermal conductivity, and moisture absorption. The effect of microcracking on failure criteria and failure modes needs to be established.

Hygrothermal Effects

As discussed in chapter 4 , the combined actions of moisture diffusion and thermal exposure (hygrothermal effects) can lead to several possible damage modes, including

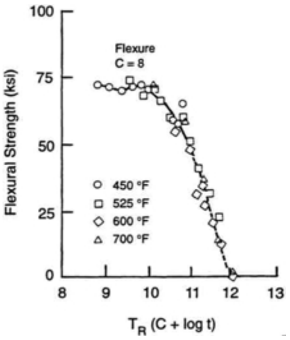

FIGURE 5-11 Correlation of room-temperature strength after various exposure times and temperatures at 760 torr. Source: Pride et al. (1968).Copyright (1968) SPI Composites Institute. Reprinted with permission.

intrinsic property loss, matrix cracking, microvoid generation, delamination, and surface blistering. Extensive work has been accomplished to understand the diffusion of moisture in composites and the resulting composite properties (Fried, 1967; McKague et al., 1975, 1978; Browning, 1978; Loos and Springer, 1979; Adamson, 1980; Wolff, 1993). These studies were, for the most part, focused on epoxy-matrix composites. Moisture effects on high-temperature polyimides have also been studied (Cornelia, 1994; Paplham et al., 1994).

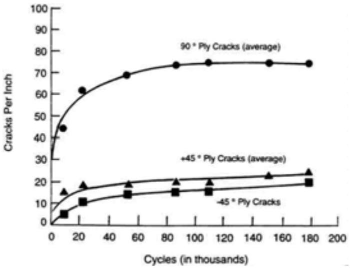

FIGURE 5-12 Damage progression of matrix cracking in a laminate versus number of cycles. Note: Data are for mechanically induced cracking (fatigue loading). Source: NRC (1991).

The diffusion models described above, based on absorption measurements on test laminates, allow diffusion rates to be described under a wide range of conditions and laminate construction. Moisture distributions and the effects of hygrothermal cycling on moisture gradients can be characterized. Work needs to be undertaken to allow prediction of residual stress and mechanical property effects from moisture concentration gradients and diffusion histories and on synergistic effects of matrix cracking and moisture absorption.

CERAMIC SYSTEMS

As described in chapter 3 and chapter 4 , the state of development of high-performance ceramic-matrix composites has not reached a point where much is known about basic materials properties, degradation methods, or the characterization and modeling of aging phenomena. This section describes testing and analytical methods that could be important in evaluating the long-term performance of ceramic composites.

Oxidation and Volatilization

The degradation mechanisms described in chapter 4 illustrate the possibility of rapid loss of a silicon-compound-based material, even when a passive SiO_2 layer forms, by the removal of hydrated silica species. The details of the effects of total pressure and gas velocity on the kinetics of the oxidation followed by volatilization must be determined. High-pressure gas burner rigs can be used for these studies but they are expensive and difficult to maintain. High-pressure TGA studies can be performed over a range of pressures and velocities to develop a model for this complex process, and the burner rigs can be used to verify the predictions of the model.

In the active regime where SiO(g) forms directly by oxidation of the substrate, the behavior at one atmosphere and in partial vacuum is well understood. Oxidation measurements at high pressure must be carried out to extend the model into the range of realistic operating conditions under fuel-rich conditions.

Thermal cycling has adverse effects on silicate scales, particularly when they begin to crystallize. Thus, the oxidation experiments enumerated above must also be carried out under conditions of thermal cycling in order to determine these effects on the oxide scales.

Mechanical Response

Behavior of the Constituents

The creep behavior of the fiber and matrix in ceramic-matrix composites can be measured in a straightforward manner. The SiC-based fibers typically show primary creep over their whole life, and phenomenological models can be accurately fitted to the data to allow interpolation and extrapolation (Jia et al., 1993; Lewinsohn et al., 1994). Similar detailed analyses must be performed on the new SiC-based fibers, such as Hi-Nicalon$^{®}$ and fibers produced by Dow Corning, and Carborundum. The matrix behavior can be measured by depositing it on a highly compliant carbon fiber and performing similar measurements to those outlined above for fibers.

The rupture behavior of these fibers at high temperature appears to be controlled by slow crack growth, but the detailed studies to correlate the experimental data with the model predictions are incomplete. DiCarlo et al. (1994) have used a phenomenological model to fit a very limited data set to attempt extrapolations into the long-lived regime. Much more extensive data generation must be undertaken to provide sufficient data to verify model predictions.

Behavior of the Composite

The complications of unstable interfaces and the lack of a large supply of the specific engineering material has hindered the determination of the time-dependent response of the composites at high temperature. Holmes et al. (1993) have shown the creep response of SiC-fiber/Si3N4-matrix composites, illustrating the characteristics of these materials when both components creep. They have also demonstrated the creep recovery characteristics of these materials. In general, SiC/SiC composites can be expected to behave similarly at higher temperatures than composites used for the silicon-nitride matrix materials. Matrix cracks will probably form in the SiC/SiC composites in use because of thermal transients and steady-state thermal gradients. Thus, the behavior of the material at high temperature in the elastic-elastic, elastic-plastic, and plastic-plastic region must be studied.

Microcomposites (single fibers or monodirectional fiber tows in the matrix) are being used to study interfaces at room temperature. Evaluation of microcomposites at high temperatures to determine interfacial properties has not been completed. Also, the effect of HSCT service conditions must be incorporated to develop a realistic appraisal of the materials in service.

Expected HSCT service conditions necessitate study of thermomechanical fatigue in simulated service environments of these composites. In conjunction with the above-listed studies of the degradation processes of the individual constituents, the thermomechanical fatigue studies should lead to an understanding of which process dominates in which regime so that material modifications can be made to defeat the degradation process.

ANALYSIS OF STRUCTURES

Current structural design and analysis procedures in the aeronautics industry make use of materials properties that are largely semiempirical, even though significant improvements have occurred in other aspects of structural analysis methodology over the last two decades (NRC, in press). The standard practice relies heavily on extensive testing at the various levels, including:

- coupon-scale tests to establish basic static and time-dependent design property limits, or allowables, under pertinent environmental conditions;
- element tests to relate allowables to design elements; and
- tests on structures from subcomponent through full-scale components culminating in static and fatigue tests on the complete aircraft to verify scaling models and assumptions.

Design details are frequently improved through test programs. Scale-up effects are handled through a building-block approach that relies on testing to verify the anticipated structural performance at each scale level.

Test methods for developing design allowables for metallic and composite structures are fairly well established and are continually reviewed by the Federal Aviation Administration through committees such as MIL-HDBK-5 for metals and MIL-HDBK-17 for composites. While test methods will continue to be refined and updated to establish more-reliable design property values and allowables, the conditions under which the values were established, including product form, processing method, and thermal treatments, is very important.

Modeling techniques are critical in relating the fundamental aging characteristics to complex structural components. The effects of scale, geometry, surface quality, coatings, and diverse individual service conditions must be considered together with their possible synergistic interactions. Analyses of mechanisms and rates of degradation must be evaluated at increasing size scales to provide technical guidance for component design and testing protocols.

Metallic Materials

Metallic materials tend to fail due to the formation and growth of a dominant microcrack (or cracks) that eventually reach a critical length and then more rapidly propagates to failure. While fracture mechanics is now a mature part of the engineering standard practice, rigorous prediction methodology only exists for brittle materials that exhibit limited plasticity. Fatigue crack growth behavior and fracture processes exhibited by ductile materials are reasonably well understood.

It is currently possible to use a deterministic approach to predict the structural durability of metallic components for high-speed aircraft. Such an approach would include stress analysis, crack initiation analysis, and crack growth analysis.

- *Stress analysis* determines stress/strain/time history in fracture-critical locations. To perform such analysis, accurate constitutive models are needed that can account for time-dependent deformation and damage response, as well as the influence of microstructural degradation under monotonic, sustained, and cyclic loading.
- *Crack initiation analysis* ensures that design-life requirements are completely met. Models for predicting crack initiation must account for all relevant damage and degradation mechanisms.
- *Crack growth analysis* provides damage-tolerance calculations and determines inspection intervals and criteria. These models must be able to account for all relevant time-dependent and fatigue-cycle-dependent modes of crack growth and include effects of environment and variable amplitude loading.

Composite Materials

In contrast to metals, composite materials exhibit complex failure modes that may involve the interaction of several different damage mechanisms. The complexity of the failure modes becomes a major design consideration when addressing durability and damage tolerance requirements. Most design allowables depend on the as-cured properties of the constituents and the fiber architecture.

The current design practices rely heavily on empirical approaches to conservatively estimate the effects of damage on durability and damage tolerance. For example, simple tests such as open-hole compression and compression-after-impact tests are often used to establish “knock-down” factors for reducing the working strain levels to avoid damage growth. In the absence of mechanics methods to predict damage initiation, growth, and failure modes, all test data must be obtained on the specific laminate stacking sequence or fiber preform architecture to be used in the design. Test data at the element and subcomponent levels are relied on to confirm the suitability of the structural design parameters to couple coupon-level material behavior and test data to the actual structural behavior.

Two methodologies used to predict remaining strength (damage tolerance) and life of composite structures are currently being integrated into design codes. The first is the use of “damage mechanics” to predict the changes in stiffness that occur during service life (Talreja, 1985; Simo and Ju, 1987; Lee et al., 1989; Shapery, 1990). This approach is becoming common for the purposes of following the development of damage and for interpreting the changes in stiffness of the structure as well as at the microstructural level in composites. The second methodology is the use of micromechanics and kinetic theory to predict remaining strength. Micromechanical representations of the fundamental composite strengths are constructed in terms of the constituents, their geometry, and their arrangement (Reifsnider and Stinchcomb, 1986; Gao and Reifsnider, 1991; Reifsnider, 1991a, b, 1992; Reifsnider and Gao, 1991; Xu and Reifsnider, 1992). The constitutive parameters in these strength models are studied as a function of the service inputs and environments using kinetic (or rate) theory allowing fatigue, creep, creep rupture, aging, oxidation, and other time-dependent and cycle-dependent effects to be introduced.

CHAPTER SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Characterization Methods

The characterization of aging responses in structural materials entails establishing the fundamental relationships between service and environmental exposure and structure and property metrics. To be useful in analytical models, the relationship between exposure and material structure or property must include methodologies to integrate degradation rates; dependence on environmental factors such as temperature, pressure, loads, or concentrations; and the effect on a significant performance metric.

Methods to evaluate fundamental materials responses are fairly well established for isolated damage mechanisms. However, the potential of synergistic effects between mechanisms is not completely understood. Unfortunately, it would be virtually impossible to explore each possible combination. Therefore, a carefully designed evaluation approach using statistical design of experiment techniques is required to determine the interactions with the greatest potential effects on in-service properties.

A critical aspect in the testing and characterization of aging response is the relation to a performance metric (most often related to mechanical properties). The degradation mechanisms described in operate over a broad hierarchy of size and time scales. It is important to test aging response at the size scale where the degradation takes place. For example, as described in chapter 4 , oxidation of polymeric composites has the most profound effect at edges and at fiber-matrix interfaces. Hence, the most sensitive measure of oxidation effects would be expected to be the degradation of the strength of the bond between the fiber and matrix resin.

The committee recommends that:

- Methods be developed to characterize aging responses in structural materials for previously identified degradation mechanisms by establishing the fundamental relationships among service and environmental exposure conditions, damage accumulation, and structure and property metrics. These relationships must include property degradation or damage accumulation rates; dependence on critical environmental factors such as temperature, pressure, loads, strain rate, concentrations of chemical agents, and synergistic effects; and effects on significant performance metrics.
- Statistical experimental design approaches be used to establish critical dependencies between degradation mechanisms.

Accelerated Methods

The long service-life requirements of HSCTs and the limited time available for development, evaluation, and validation of material candidates makes acceleration of aging characterization methods necessary. Accelerated exposures and testing can be accomplished through a number of schemes, depending on the aging mechanisms and the environmental variables. In many cases, it may be possible to accelerate exposures or tests by increasing exposure temperature, increasing loads, predamaging test articles, shortening hold times on cyclic exposures, or increasing the concentration of a degradative chemical or compound. When using accelerated exposures, it is necessary to anticipate and avoid excursions into or near regimes where other degradation mechanisms are expected to become active.

Accelerated methods become much more complex when multiple mechanisms and synergistic effects are involved because the relationship between accelerated and service conditions is not usually the same for different mechanisms. For this reason it is very difficult to directly test multiple accelerated conditions simultaneously. The committee concludes that the most viable approach to the characterization of multiple aging mechanisms is to incrementally subject samples to accelerated conditions designed to advance single-failure mechanisms. Samples would be cycled through a series of conditions designed to advance different discrete mechanisms, in turn, until end-of-life conditions are reached.

The committee recommends development of:

- accelerated exposure and test methods, with calibration to service conditions or end-of-life microstructural conditions, for critical degradation mechanisms, and
- testing and exposure approaches that allow incremental application of conditions to evaluate multiple, synergistic degradation mechanisms.

Analysis of Structures

The potential degradation of mechanical properties as determined from materials aging-response characterizations and the potential for damage accumulation over the service life must be considered when developing design property test programs and protocols for structural components. Durability predictions can be verified using controlled, real-time tests and accelerated methods. While beyond the scope of the current study, it may be of interest to compare laboratory simulations with service experience for established materials such as alloys for power generation applications (see Figure 5-3 and Figure 5-4) and first-generation aircraft materials (especially 7XXX-series aluminum alloys and carbon/epoxy composites).

Monitoring of service components provides information useful to validate aging methods and predictions. Validation of service condition assumptions, characterization test results, and model predictions can be based on monitoring of fleet-leading aircraft. Service monitoring can be accomplished using visual inspections and nondestructive evaluations as part of the airlines' maintenance program or by performing destructive mechanical and microstructural evaluations. Nondestructive evaluations would be used to detect unanticipated damage. Unfortunately, available techniques—currently effectively limited to optical, radiographic, and ultrasonic methods—have limitations due to poor structural inspection standards, inadequate defect indication interpretation, poor reliability, high cost, and inadequate linkage between design analyses and nondestructive evaluation results (NRC, in press). Rapid, wide-field nondestructive evaluation methods that can account for limited or one-sided access are needed to effectively monitor in-service components. Destructive evaluations would determine the type and extent of changes in properties and microstructure, and the type size, and distribution of deformation and fracture damage.

The committee recommends that:

- An integrated modeling capability be developed to relate characterizations of materials aging responses to component performance. An ability to examine the effects of scale, geometry, finishes, and individual service conditions must be part of the model specifications.
- Property degradation and damage accumulation be included as part of component durability evaluations and be considered in the design property test programs and protocols.
- Model predictions be verified using controlled realtime tests and accelerated exposure and test methods.

Approach to Materials Aging Characterization

The committee believes that an approach based on a fundamental understanding of materials response, degradation methods, and models and simulations based on validated accelerated test methods will lead to increased confidence in aging predictions. Regardless of the material system or application, the committee suggests that the fundamental approach to the characterization of aging behavior should be the same. The approach that the committee recommends is depicted schematically in Figure 5-13.

In the case of high-speed aircraft applications, several organizations have roles in the characterization of aging phenomena. The aircraft manufacturers should define the data needs and service conditions, apply analytical techniques to predict the aging response at the component level, and validate model predictions against controlled real-time tests. The material suppliers and academic researchers should perform the systematic characterization of materials properties and aid in the identification of potential degradation mechanisms under the full range of service and test conditions.

The materials and degradation mechanisms that should be emphasized by NASA for the HSCT depends on the design speed chosen. For the airframe of the current baseline aircraft (Mach 2.4), matrix cracking, thermal degradation and oxidation, and hygrothermal degradation and microstructural stability of high-temperature thermoset- or thermoplastic-matrix composites and microstructural effects, hydrogen embrittlement, and moderate-temperature effects (strain aging, slip localization) of titanium alloys should be emphasized. For the airframe of a Mach 2.2 aircraft, elevated-temperature fatigue, creep, environmental effects, and microstructural stability of high-temperature ingot aluminum alloys could be considered. For engine materials, low-cycle fatigue, creep, oxidation, and microstructural stability of nickel-based superalloys and thermochemical degradation (including corrosion and oxidation reactions) effects on slow crack growth and creep deformation in ceramic-matrix composites should be emphasized.

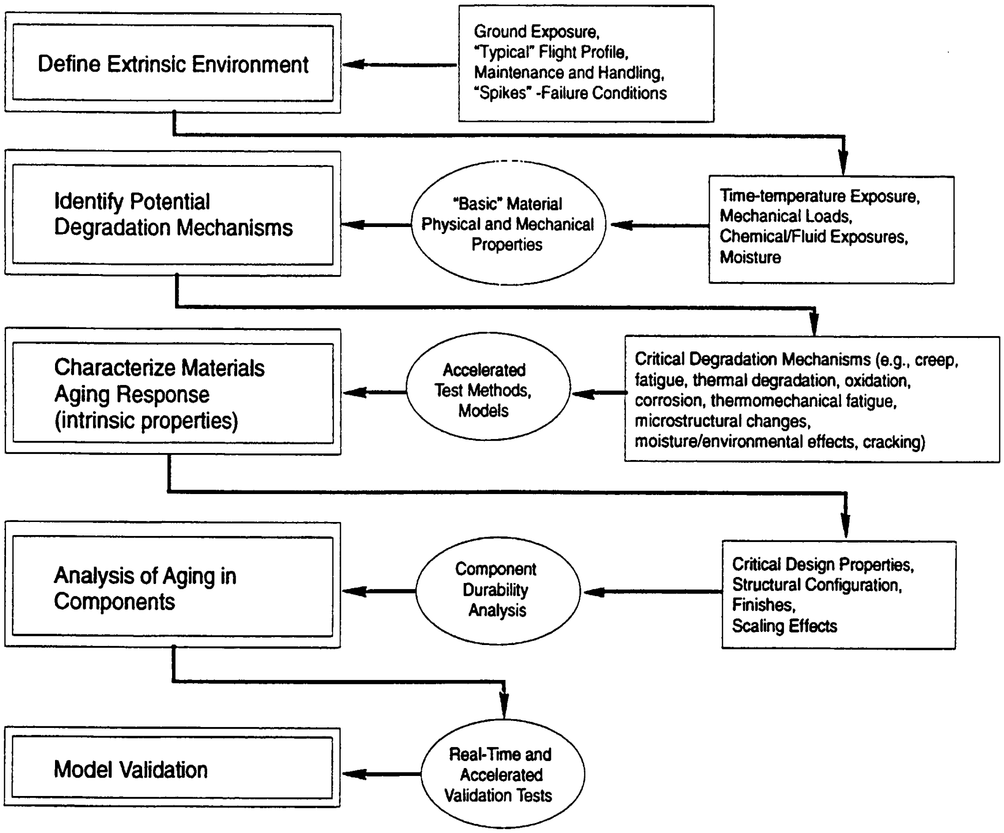

FIGURE 5-13 Recommended general approach to characterization of aging of materials and structures.

The committee recommends that:

- NASA (1) integrate the efforts to provide fundamental characterization of materials properties, degradation mechanisms, and aging responses, and (2) develop the modeling capability to relate aging responses to component performance.

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Appendix

Biographical Sketches of Committee Members

EDGAR A. STARKE, JR. (Chair), received a Ph.D. in metallurgical engineering from the University of Florida. He has held positions at DuPont's Savannah River Laboratory, and at the Georgia Institute of Technology and the University of Virginia where he served as dean of engineering and applied science. He is currently the Earnest Oglesby Professor of materials science at the University of Virginia. Dr. Starke's research is in advanced alloy development, fatigue and fracture, and high-temperature aluminum alloys. He is a member of the National Materials Advisory Board of the National Research Council.

RICHARD H. CORNELIA received a Ph.D. in organic chemistry from Oregon State University. He is currently a senior research associate in the Advanced Composites Division of the DuPont Company. His expertise is in high-temperature polyimides, composite mechanical properties, carbon fiber properties and performance, high-temperature fiber sizing, high-temperature adhesives, and fractography.

LONGIN B. GRESZCZUK received an M.S. in structural engineering from Purdue University. He is currently senior staff manager and MDC Fellow at McDonnell Douglas Astronautics Company. His experience has been in theoretical and experimental research in composite micromechanics and macromechanics of composite materials and structures.

LYNETTE M. KARABIN received a Ph.D. in materials science and engineering from Northwestern University. She is currently a technical specialist in Alcoa's Alloy Technology Division. Her research concerns the development of new heat-treatable alloys and optimization of existing alloys for aerospace.

JOHN J. LEWANDOWSKI received a Ph.D. in metallurgy and materials science from Carnegie Mellon University. He is assistant professor in the Department of Materials Science and Engineering at Case Western Reserve University. His research is in the effects of microstructure on deformation and fracture of materials.

ASHOK SAXENA received a Ph.D. in materials science and metallurgical engineering from the University of Cincinnati. He is currently director and professor of the School of Materials Engineering and director of the Composites Education and Research Center at the Georgia Institute of Technology. His research is in time-dependent fracture mechanics, microstructure property relationships, creep, and creep-fatigue crack growth, and composite materials.

JAMES C. SEFERIS received a Ph.D. in chemical engineering from the University of Delaware. He is Boeing/Steiner Professor of polymeric composite materials at the University of Washington. His interests are in polymer composites, matrix polymers, polymer/composite processing, environmental durability, and thermal analysis.

RICHARD E. TRESSLER received a Ph.D. in ceramic science form the Pennsylvania State University. He is head of the Department of Materials Science and Engineering at Pennsylvania State University. His research concerns the fabrication and mechanical behavior of structural ceramic and composite materials and fracture and strengthening mechanisms.

DOUGLAS D. WARD received an M.S. in materials science from the University of Dayton. He has worked at the Garrett Turbine Engine Company and is currently technical team leader for polymeric composite applications in the Engineering Materials Technology Laboratory at GE Aircraft Engines. His experience includes characterization of high-temperature polymeric composites for commercial and military aircraft applications.