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Thrust Area Report FY 92
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Materials Science and Engineering

Donald R. Lesuer

March, 1993

Lawrence
Livermore
National
Laboratory

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Materials Science and Engineering

Donald R. Lesuer

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Materials Science and Engineering

The objective of the Materials Science and Engineering thrust area is to enhance our understanding of the physical and mechanical behavior and the processing/structure/property correlations for structural materials that are of interest to Lawrence Livermore National Laboratory (LLNL) programs and U.S. industry. We also seek to enhance our ability to model the processing of these materials using LLNL's finite element codes. Our activities are currently focused on composite materials, superplasticity, and process modeling.

Composite Materials

Our work in composite materials is directed toward polymer matrix composites and metal matrix composites. LLNL has a long history of achievements in the investigation of polymer matrix composites. These materials have received considerable research attention and product application at LLNL and in industry because of their unique properties, including high specific strength, high specific stiffness, composition of low Z atoms, corrosion resistance, and the possibility for a low coefficient of thermal expansion. These properties can also be tailored to specific applications. During FY-92, we have focused on studying the three-dimensional mechanical response of continuous fiber, polymer matrix composites. These studies have significantly enhanced our understanding of the response of these materials and our ability to test and model this behavior using finite element codes. During FY-92 we have also studied the use of laser Raman spectroscopy

to monitor *in situ* the state of cure in polymer matrix composites.

We also work on metal matrix composites (MMC's), which are materials of choice in applications requiring high specific strength and stiffness. These materials can have excellent thermal and electrical conductivity and, depending on the alloy matrix, excellent high-temperature behavior. During FY-92, we studied the processing/structure/property correlations in a unique form of MMC, called a laminated metal composite, in which alternating metallic layers are press-bonded together.

Superplastic Materials

Superplastic materials are crystalline solids that can be deformed in tension to such an extent that large strains will be attained at very low flow stresses. These materials, which deform like hot glass, permit components to be formed into shapes, the dimensions of which are very close to those desired in the final product ('net shape processing'). Thus, machining and machining-related operations can be reduced or eliminated. Our work in this technology has been stimulated by U.S. industry, which has demonstrated a strong interest in superplasticity for net shape processing. Currently, LLNL is engaged in two collaborative research and development projects with industry in the area of superplasticity. One project, with three partners, is developing the technology for commercial production of superplastic, ultra-high-carbon steels. Another project is developing a superplastic aluminum alloy with a faster forming rate and the capability for diffusion bonding. Su-

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perplastic forming can also reduce environmental, safety, and health problems in the Department of Energy nuclear weapons complex through the reduction of toxic and radioactive scrap produced during the fabrication of components. This year the thrust area has been studying the microstructural changes that take place during superplastic deformation. A model is being developed for use in LLNL's finite element codes that will account for the influence of material microstructure and its evolution on the stress-strain-strain rate behavior of superplastic materials.

Process Modeling

Our work in process modeling is inspired by the enormous impact of this technology on economic manufacturing competitiveness and by the unique opportunities for LLNL to assist industry, given its extensive experience with modeling problems and its extensive computational resources and codes. Researchers within this thrust area are enhancing the capability of LLNL codes to model the casting process. Casting is a common industrial manufacturing process that is also very complex and influenced by many process and component variables. For these reasons, finite element modeling is a very powerful tool for understanding and predicting the success or failure of industrial casting operations. Work is continuing on a unique fluid-thermal-stress finite element code that will predict the final shape and stress state of precision cast parts.

Donald R. Lesuer
Thrust Area Leader

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Donald R. Lesuer, Thrust Area Leader

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Processing and Characterization of Laminated Metal Composites

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We have made laminated metal composites of (1) ultrahigh carbon steel (1.8% C) and brass (70% Cu-30% Zn), and (2) Al 5182 and Al 6061-25 vol % SiC_p. The laminates were prepared by hot pressing alternating layers of the component materials in an argon gas atmosphere. Tensile and fracture toughness were measured for different processing conditions of surface oxide descaling, layer thickness, and heat treatment. Descaling of the surface oxide prior to the press-bonding was found to eliminate premature delamination along interfaces, resulting in an increased yield strength and tensile ductility. Reduction in the layer thickness brought a large increase in tensile ductility, and a small decrease in yield strength and fracture toughness. T6 heat treatment on the Al laminates induced a substantial increase in the yield and tensile strength, but a decrease in tensile ductility. Fracture toughness measured both in the crack-arrester and crack-divider orientations showed a large enhancement over that of the component materials. Damping capacity measurements also showed rather remarkable increases over that of the component materials.

Introduction

The idea of laminating different metals and alloys to form a composite material that exploits the good properties of the constituent materials has been known from antiquity: *The Illiad* of Homer, e.g., describes Achilles' shield, made of two outer layers each of bronze and tin and one middle layer of gold.¹ The idea has also been used in many industrial applications.² However, most of the current industrial metal-based laminates contain only two or three layers, and are used to save material cost while maintaining required wear or corrosion resistance. Recent studies^{3,4,5} show that multilayer laminated metal composites (LMC's) can have superior damage-critical properties such as fracture toughness and fatigue resistance, over that of the component materials. Damage crack propagation in a laminate of dissimilar materials is inherently difficult, since an interface can act as a barrier to the crack propagation, especially when such an inter-

face delaminates at the crack tip and blunts the crack.⁶ Studies^{3,4,5} also show that it is possible to design a LMC with given performance character-

Figure 1. An example of as-pressed Al/Al-SiC_p laminate after the edges were trimmed.

Table 1. Tensile properties of Al 5182/Al 6061-25 vol% SiC_p.

Processing	Layer Thickness, μm	Yield Strength, MPa(ksi)	Ultimate Tensile Strength, MPa(ksi)	Elongation, %
Scale Not Removed	750	138(20.0)	262(38.0)	10.0
Descaled	750	162(23.5)	266(38.5)	16.9
Descaled, T6	750	232(33.6)	333(48.2)	7.2
Descaled, Re-pressed, T6	100	201(29.2)	324(47.0)	12.0

istics, through the choice of component materials, number of layers, thickness of the layers, and interfacial bond strength. A good example is the LMC formed by press-bonding alternate layers of ultra-high carbon steel (UHCS) and mild steel. In this LMC, the dynamic fracture toughness is far higher

than that of either of the component materials. LMC's can also have damping capacity superior to that of the component materials, which can be very useful in structures requiring high acoustic damping.

Progress

We initiated the present research in FY-91⁷ to investigate the influence of processing and structural variables on the mechanical properties of multilayer LMC's made of two constituent materials, one ductile but tough and the other brittle but strong. We chose in FY-91 to study two LMC systems, UHCS/brass and Al/Al-SiC_p, and continued this study in FY-92. These two systems were chosen to show that the toughness at ambient temperature of hard and brittle UHCS and Al-SiC_p can be enhanced substantially by lamination with ductile but tough counterparts. The main thrust for FY-92 was to study the influence of the surface preparation of the component materials and the layer thickness of the laminates on their interfacial microstructure and mechanical properties.

Experimental Procedure

Materials and Processing. UHCS of a nominal composition of Fe-1.8% C-1.65% Al-1.5% Cr-0.5% Mn was preprocessed⁸ to have a fine-grained ferrite matrix of about 0.5- μm grain size and spheroidized iron carbides on grain boundaries. Brass (70% Cu-30% Zn), Al 5182 (Al-4.5% Mg-0.35% Mn), and Al-SiC_p [Al 6061 (Al-1.0% Mg-0.6% Si-0.28% Cu-0.2% Cr) matrix with 25 vol.% SiC particulate] were obtained from commercial sources.

All materials were sliced to 50 mm-x-50 mm squares. Al 5182 and Al 6061-SiC_p squares were descaled using an acid solution. UHCS and brass were surface-machined and degreased. A lami-

Figure 2. (a) Optical and (b) scanning electron microscope microstructure in the vicinity of an interface in Al/Al-SiC_p laminate.

nate containing an equal volume fraction of the two component materials was prepared by hot-pressing a stack of alternate layers of the components. Each stack was pressed to one third or one fourth of its original height. Such a large reduction ensured good bonding at interfaces. UHCS laminates were press-bonded at 750°C, and Al laminates at 450°C. Some laminates were sliced into four equal-sized pieces, re-stacked, and re-pressed to obtain laminates with reduced layer thickness. Average layer thickness was about 750 μm for both laminates after initial pressing; about 200 μm for UHCS and 100 μm for Al laminates after re-pressing. Some Al laminates were given the T6 heat treatment for the Al 6061 matrix of the Al-SiC_p component.

Testing. Tensile tests were performed with flat specimens cut with the tensile axis parallel to the layers. Fracture toughness was measured with chevron-notched short bar or three-point bend bar specimens in which the notch was cut either in the crack arrester or crack divider orientation. In the crack arrester orientation, the crack front propagates in the thickness direction, cutting the layers sequentially. In the crack divider orientation, the crack front propagates through the laminate, cutting all the layers simultaneously. Damping capacity along the thickness direction of the laminates was evaluated by a pulse-echo method for the ultrasonic frequency range, and by a torsion bar technique for the 0.1 to 100 Hz range.

Experimental Results

Interfacial Bonding and Microstructure. The Al laminates that were chemically descaled and the UHCS laminates whose layers were surface-machined prior to the press-bonding were well bonded and did not show any sign of interfacial delamination during machining of test specimens. A typical well-bonded as-pressed Al laminate, after its edges were trimmed, is shown in Fig. 1. Figure 2 shows an interface in the Al laminate shown in Fig. 1, both in (a) optical and (b) scanning electron microscope photomicrographs. No interfacial pores or unbonded areas, and no secondary phases are visible, indicating that no reaction between the component materials occurred.

Tensile Properties. Tensile properties of UHCS laminates were included in our FY-91 report.⁷ Summarized in Table 1 and Fig. 3 are the tensile properties for the Al laminates in the as-pressed, and T6 heat-treated conditions. For the T6 heat-treated condition, laminates with two different average layer thicknesses (750 μm and 100 μm) are com-

Figure 3. Tensile stress-strain behavior of Al/Al-SiC_p laminate. Results shows the influence of surface descaling, heat treatment, and layer thickness.

pared: the 750- μm -layer thickness material was obtained from the initial pressings, and the 100- μm -layer thickness material was obtained from re-pressings as described earlier.

Table 1 clearly shows the effect of surface oxide removal for two 750- μm -layer laminates. Descaling of the constituent materials led to a noticeable increase in the yield strength, from 138 MPa (20 ksi) to 162 MPa (23.5 ksi), and to a very substantial increase in ductility (by almost 7%), from 10% to 16.9%. No significant change in the ultimate tensile strength was observed. Figure 3 shows that the descaling treatment increases the flow stress over the entire strain range, most likely as a result of good bonding between the constituent layers, which prevents premature delamination. The importance of preventing delamination can probably be traced to the fact that in these materials, flow localization precedes fracture. Good bonding inhibits flow localization in the less ductile layers, which in turn results in greater elongation (and higher strength) before fracture.

Heat treatment considerably influences the mechanical properties, as shown by the results in Table 1 for 750 μm -layer laminates. The T6 treatment increased the yield and ultimate tensile strength by about 70 MPa (10 ksi), but reduced the total elongation drastically, from about 17% to 7%. Figure 3 shows that the flow stress was also increased.

Reduction of the layer thickness affects the tensile properties significantly. When the layer thickness was reduced from 750 μm to about 100 μm under the T6 heat-treated condition, the yield strength was decreased slightly, but the total elongation was increased rather remarkably, from 7.2% to 12%. No significant change in the ultimate tensile strength was observed. A similar strong corre-

Figure 4. Fracture toughness measured (a) for the different layer thicknesses in UHCS/brass laminates and (b) for different processing conditions in Al/Al-SiC_p laminates. The inset drawings (c) define the crack divider (C.D.) and crack arrester (C.A.) orientations used in the fracture toughness tests.

lation between the layer thickness and ductility has been observed in the UHCS laminates, as reported in FY-91.⁷

Fracture Toughness. Results of fracture toughness tests are summarized in Fig. 4 for both UHCS and Al laminates. For laminates of both systems, it is clearly demonstrated in Fig. 4 that the lamination of a hard material (UHCS or Al 6061-SiC_p) with a ductile material (brass or Al 5182) results in substantial enhancement of toughness.

For UHCS/brass, the laminates with thin (200 μm) layers show slightly lower toughness than the laminates with thick (750 μm) layers regardless of the specimen orientation, i.e., crack arrester or crack divider, relative to the layers. This trend could be due to the influence of the interfacial delamination on crack growth. Studies have shown that the delamina-

tion tendency decreases with decreasing layer thickness.⁹ Thus, it is likely that the higher toughness in the thick-layer laminates could be due to the blunting of an advancing crack by delamination. It is interesting to note, however, that delamination reduces the tensile ductility and strength, as observed for the tensile properties.

Interfacial delamination was observed also in the Al laminates regardless of the descaling or T6 treatment. The descaling treatment, however, led to an increased fracture toughness (measured in the crack divider orientation), as shown in Fig. 4, while the T6 treatment led to a reduced toughness (as measured both in the crack arrester and divider orientations). The beneficial effect of the descaling treatment results from the controlled and timely delamination of an interface as a crack approaches the interface. In the laminates made without the descaling treatment, delamination was extensive and occurred rather prematurely. The increased yield strength and reduced tensile ductility upon T6 treatment, as shown in Fig. 3, were reflected in the reduced fracture toughness, a trend observed similarly in most monolithic materials.

Damping Capacity. Damping capacity was measured only in the as-pressed condition, where the layer thickness was 750 μm for both UHCS/brass and Al laminates. At low frequencies, damping in the UHCS/brass laminate was two to three times the damping typically observed in brass or steel, and was lowest at 2 Hz. Ultrasonic attenuation measurements of longitudinal waves showed that at 2.25 MHz, the UHCS/brass laminate had an attenuation coefficient of 160 dB/m, over 12 times the attenuation coefficient for the steel component and over four times the attenuation coefficient of the brass component.¹⁰ The ultrasonic attenuation coefficient for the Al/Al-SiC_p laminate (266 dB/m) was greater than that for the UHCS/brass laminate. These results clearly show that LMC's can be more effective damping materials than their components.

Future Work

We are continuing to characterize the UHCS/brass and Al/Al-SiC laminates regarding their (1) damping capacity in the audible frequency range, (2) fatigue behavior, (3) response to ballistic impact, and (4) deformation behavior at elevated temperature. We are planning to make LMC's of other light materials such as Mg alloys, (a) containing a high damping capacity material as a component and (b) containing an intermetallic or superalloy as a component. These new lami-

nates will be tested for their strength, ductility, toughness, and other characteristics reported here for the UHCS/brass and Al laminates.

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We sincerely appreciate assistance provided by Chris Steffani for descaling Al alloys; Ralph Otto and Bill Stutler for pressing laminates; Dick Sites for preparing test samples; Al Shields for conducting mechanical property tests; and Jim Ferreira for metallography.

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Casting Process Modeling

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In predicting the quality of a cast part, two important factors are (1) correct modeling of the fluid flow and heat transfer during the filling of a mold with a molten metal, and (2) the thermal-mechanical physics of solidification and cool-down. Determining the dynamics of the flow and the free surface shape during filling are essential in establishing the temperature gradients in the melt and in the mold. Correctly modeling the physics of volume change on solidification, shrinkage on cooling, and contact resistance across the part-mold interface directly affects the cooling rate and, ultimately, the final cast shape and stress state of the cast part. This year our efforts were focused on modeling fluid fill and on the physics of solidification.

Introduction

Casting manufacturing covers a broad range, from the large tonnage of continuously cast steel products, through the intermediate-weight output of superalloy precision die castings, to the relatively small quantity of high-purity crystals. Although this project benefits modeling efforts in each of these three casting areas, we have focused on modeling precision die castings of superalloy parts.

Our approach to casting process modeling is

to use the computational fluid dynamics code ProCAST¹ to model elements of the mold-filling process, including tracking of (1) the free surface of the molten metal as it rapidly fills the mold; (2) solidification on the walls of the mold; (3) temperature transients in the mold; and (4) temperature transients in the liquid and solidifying metal. When the mold is completely filled with liquid metal, the existing temperature field at that instant in time is re-mapped (using REMAP²) onto a new mesh for a CAST2D³ analysis to predict the final cast shape, stress state, and defects.

Figure 1. Experimental (a, b, c) and numerical (d, e, f) results for the filling of a spherical annulus mold, with a liquid metal at 0.6, 0.9, and 1.5 s, respectively.

Figure 2. (a) CAST2D calculations at an early time during cool-down, showing the heat flow paths to be radially outward. (b) At later times: gaps between the casting and mold appear due to the -6.6% volume change of the aluminum casting on solidification and shrinkage on cool-down. (c) The direction of the heat-flux vectors, changed due to the part shrinking away from the mold on solidification. The heat-flux vectors are seeking the path of least resistance to heat flow.

CAST2D models the thermal-mechanical response during cooling to room temperature including volume change on phase transformation. CAST2D also calculates thermal contact resistance across the part/mold interface.

Progress

An experimental and numerical analysis was performed to investigate the filling of a spherical mold with a liquid metal. The experiment provided visual data of the filling of the shell for comparison with the numerical calculations. The die-casting process consisted of pressurizing a pool of molten metal in a crucible and forcing the melt up a small tube to be injected into the bottom of a spherical annulus-shaped cavity. The experiment was conducted in a vacuum. The experimental data consists of a 16-mm motion picture (24 frames per second) of radiographs of the filling of the spherical annulus. The spherical annulus filled in approximately four seconds. **Figure 1** shows radiographs at three different times during the filling process. The radiographs show that initially the melt splashes fairly high up the annulus (**Fig. 1a**) in a nonsymmetric fashion. Although still showing considerable wave motion at later times (**Fig. 1b**), the melt is seen to be filling the annulus in a more symmetric fashion. At still later times, the fill level advances evenly and symmetrically up the annulus (**Fig. 1c**).

ProCAST was used to numerically model the mold filling process. The spherical annulus was modeled as a two-dimensional, axisymmetric problem. Fluid properties, i.e., density, specific

heat, and viscosity, were allowed to be functions of temperature. Results of the analysis are presented in **Figs. 1d, 1e, and 1f**. These three figures show the free surface and level of fill at the same times as the experimental results. The numerical analysis does not show the wave motion and non-symmetry at early times as observed in the experiment. However, it does show the wall jet effect as the melt enters the annulus (**Fig. 1d**) and a fill level that is near the average level of the experiment (**Fig. 1e**). At later times, when the flow is more even and symmetric, the analysis compares favorably with experiment (**Fig. 1f**).

We performed a fluid-thermal-mechanical analysis of the casting of a three-spoke, 38-cm-dia aluminum wheel. The liquid aluminum at 780°C was injected into the steel mold, which is heated to 730°C , at a rate that fills the mold in two seconds. By forced convection, the outer surface of the mold lost heat to the environment. ProCAST was used to model the fluid-filling process. When the mold was completely filled with liquid metal, the existing temperature field at that instant in time was re-mapped onto a new mesh for a CAST2D analysis. CAST2D was used to model the thermal-mechanical response during cooling to room temperature. The aluminum undergoes phase change at 660°C with a volume change of -6.6% . The aluminum part is in good contact with the mold at early time. The heat flux vectors are seen to go radially outward (**Fig. 2a**) through the aluminum part and mold to the environment. At a later time, the aluminum has shrunk away from the mold due to volume shrinkage on solidification, and gaps have opened up (**Fig. 2b**). The heat-flux paths

shown in Fig. 2c are seen to be considerably changed from the pattern of Fig. 2a. The direction of the heat-flux vectors has changed while seeking the path of least resistance to heat flow.

Future Work

In the future, we plan to develop a closely coupled fluid-thermal-mechanical code to be used for analysis of casting problems. Numerical modeling in the areas of fluid fill, solidification physics, and material constitutive development must be refined for such a code to be useful in casting process modeling. We

also plan to conduct experiments for code validation.

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Characterizing the Failure of Composite Materials

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Our goal for this project has been to characterize the three-dimensional (3-D) performance of continuous-fiber polymer composite materials, by developing new experimental and theoretical methods. This report highlights our major accomplishments: (1) multiaxial testing of composites; (2) the development of a new composite-failure criterion; (3) the development of ORTHO3D, a 3-D orthotropic finite element code; (4) the dynamic testing of composites; and (5) a helical compression study of filament-wound composite tubes.

Introduction

This project has helped to develop carbon-fiber composite materials for use in penetrating warhead cases, gun barrels, advanced munition components, projectiles, nuclear weapons, SDI, and high-energy-density flywheels.

We have had the opportunity to jointly pursue some of this work with various research and development centers of the U.S. Army and Navy, as well as with various contractors in private industry. The primary reason for selecting carbon-fiber composite materials is their high specific strength and stiffness. Other factors influencing design include low 'Z' material composition, low coefficient of thermal expansion, impact resistance, and fire safety.

These materials are generally limited not by their performance capabilities but by our lack of understanding and ability to model their complex 3-D response. Our research effort has made great strides in providing the necessary tools and information to optimize these designs.

Progress

Our major accomplishments have been (1) multiaxial testing of composites; (2) the development of a new composite-failure criterion; (3) the devel-

opment of ORTHO3D, a 3-D, orthotropic finite element code; (4) the dynamic testing of composites; and (5) a helical compression study of filament-wound composite tubes.

Multiaxial Testing of Composites

Our most important accomplishment has been the development of a unique multiaxial test system

Figure 1. Multiaxial test system for composite tubes.

Figure 2. Load description for multiaxial test specimen.

Figure 3. Multiaxial failure surface for a filament-wound Toray 1000/DER332-T403 [± 1.5 , ± 45 , ± 89] carbon/epoxy laminate.

for polymer composite materials.¹ This technique allows testing of 2-in.-dia composite tubes under a combination of axial, torsion, and internal pressurization. The unique advancement with this system is the simple but effective gripping mechanism that incorporates a 15°-potted epoxy cone for providing a smooth transition in load between the grip and the test specimen. The test specimen itself is a straight-walled composite tube. Diagrams of the multiaxial grip and test specimen are shown in Figs. 1 and 2. This test system has provided Lawrence Livermore National Laboratory (LLNL) with an unrivaled capability to generate multiaxial failure data for polymer composite materials.

The most extensive multiaxial failure surface that was generated with this system is shown in Fig. 3. The material system used in this study consists of the Toray 1000G carbon fiber having a 950-ksi tensile strength, impregnated with DER332-

T403 epoxy having a tensile strength of 10 ksi. This material system has been used in the majority of the composite structures we have designed and fabricated.

The multiaxial gripping concept has led to the development of an efficient high-strength shear joint for split composite pressure vessels and for modular composite gun barrels. We have also successfully scaled up the gripping system to test 9-in.-dia composite tubes under axial load. The biggest use of this system, however, has been focused on the optimization of the compression performance of filament-wound tubular structures, such as those used for composite penetrators, projectiles, and support structures.

New Composite-Failure Criterion

In this project, we have developed a new failure criterion for composite materials, the 'Feng failure criterion.'² The failure criterion is written in terms of the strain invariants in finite elasticity. These invariants are written as functions of the Cauchy strains and the deformation gradients. Among these strain invariants, two are functions of the fiber orientation, and three are not. Therefore, the failure criterion can be further divided into two modes, the fiber-dominated failure mode and the matrix-dominated failure mode. The criterion contains five failure material constants for infinitesimal, general, 3-D strain states.

In the criterion, there are three quantities governing the failure surface in composites: the distortional energy, the dilational energy, and the difference between compressive and tensile strengths. The minimum number of constants required is three for each failure mode. Therefore, this failure criterion represents the minimum number of constants required for determining the failure surface of composites for the second-order strain-failure criterion.

We have previously obtained the unidirectional lamina failure surface for Toray 1000/DER332-T403 carbon/epoxy fiber composites.³ In this project, we have obtained experimentally the fundamental material properties for this unidirectional composite, both elastic constants and strength. The corresponding strengths obtained by the Feng failure criterion for symmetrically balanced angle-ply laminates, is shown in Fig. 4. The results show that the Feng criterion predicts the fiber- and matrix-dominated failure modes. Furthermore, for Toray 1000/DER332 symmetrically balanced angle-ply laminates subjected to uniaxial load, the initial failure consistently initiates in the matrix.

Development of ORTHO3D

During the second year of this program, we began an effort to develop a simple, 3-D, orthotropic finite element program for the evaluation of composite failure criteria. This algorithm has become known as ORTHO3D and has been developed under a university contract with Texas A&M University.⁴ In all, five failure criteria have been implemented: maximum stress, maximum strain, Tsai-Wu, Hashin, and the Feng failure criterion.

To perform accurate failure modeling of a laminated composite structure, ORTHO3D was written to permit detailed sub-lamina (single-ply) analysis of generic structures such as cylinders and cubes. These two generic shapes represent characteristic local volumes of larger structures such as penetrator missile cases or thick laminated plates. Performing this level of analysis explicitly with NIKE3D or DYNA3D is too cumbersome to be cost effective. Furthermore, large structural analysis codes like NIKE cannot simultaneously model the global behavior of a structure and model the characteristic local volume in sufficient detail to perform accurate local-failure analysis (local/global modeling).

ORTHO3D, which is written in Fortran, is operational on a variety of computer platforms, including Macintosh, SUN, Vax, and IBM. The size of problems (local volume) that one can solve is limited only by computer memory. Even small local volumes require an astonishingly large amount of memory. Typically, a single ply is 0.005 in. thick, and the local volume is composed of many of these layers. Generally, we recommend a minimum of three elements (8-noded brick elements) through the thickness of each ply to capture representative local stress/strain behavior. Maintaining a respective aspect ratio (< 10) for each element, the number of elements required to model a local volume can be very large. At 8 nodes per element and 3 degrees of freedom per node, the memory requirements can quickly exceed most small computers. Typical local volumes that we have solved require ~ 20 Mb of ram. Efforts over the last year have focused on minimization of memory requirements via more efficient equations solvers, nodal number schemes, and array sharing.

To facilitate the 3-D modeling of composite structures, ORTHO3D was adapted to generate the effective, 3-D, homogenized properties for the characteristic local volumes required by NIKE for analysis of large (global) composite structures. The homogenized 3-D properties are considered more representative of the actual structural behavior of

Figure 4. Failure strengths predicted by the finite-strain-invariant failure criterion for Toray 1000/DER332 symmetrically balanced angle-ply laminates.

Figure 5. High strain-rate-bearing compression of IM6/974 [0,90] tapered cubes.

the local volume than those properties predicted by available, 3-D, micromechanical constitutive solutions. Once NIKE solves the structural problem, the local traction set can be passed to ORTHO for detailed failure analysis.

Dynamic Testing of Composites

To provide design support of the composite penetrators, gun barrels, and projectiles being developed at LLNL, we have evaluated and developed a variety of new high-strain-rate testing techniques for polymer composite materials.⁵ Prior to this investigation, an extremely limited data set was available on the high-strain-rate response of polymer composites. We have successfully generated strain rate data from 0/s to 3000/s in compression and 0/s to 100/s in tension, using a variety of test machines. Our ef-

Figure 6. Strain rate sensitivity of the average modulus for DER332-T403 epoxy.

Figure 7. Strain rate sensitivity effects on the compressive flow stress for three epoxy resins.

forts have yielded some very interesting and encouraging material responses.

Most of our efforts focused on developing an acoustically damped, high-energy drop tower for evaluating the high-strain-rate compressive performance of composite materials. Three major advances occurred to the drop tower system that created a highly capable material-evaluation system. First, an acoustically damped base system was installed that eliminated spurious shock waves

that were convolved with the quartz load cell data. Second, a high-speed data-acquisition system was developed that significantly automated data gathering and reduction. Third, a precision alignment fixture was developed along with precision-machined test specimens, which resulted in a significant improvement in the measured mean strength of the composite materials as well as minimized data scatter.

Three interesting results from our efforts are presented. All of our experimental results indicate an increase in both strength and modulus with increasing strain rate. First, the bearing compression strength of a [0,90] laminated composite material is presented in Fig. 4. This result reveals a significant strengthening occurring at strain rates above 10/s. An examination of neat resin behavior revealed similar trends. Figure 5 shows the change in neat resin modulus as a function of strain rate. Finally, Fig. 6 shows strain-rate sensitivity effects on the compressive flow stress of three different epoxy resin systems being evaluated at LLNL.

Helical Compression Study of Filament-Wound Composite Tubes

During the last year of this program, an evaluation of the compressive performance of helically wrapped carbon/epoxy tubes⁶ was performed using the three different epoxy resins shown in Fig. 6. The objective of this study was to optimize the compression performance of filament-wound composite structures. Table 1 lists the basic properties of these systems that influence the compression strength of composites. The last two columns in Table 1 are processing parameters.

The compressive strength of a unidirectional composite material is controlled by the properties of the matrix surrounding the fibers. It has been argued that compression of unidirectional composites is a micro-buckling controlled event in the fibers, and thus dependent on factors such as the local shear modulus of the matrix. What we were hoping to find was an improvement in compression strength of helical composite tubes fabricated with the MY0510-HY350 epoxy system.

Figure 8 shows the variation in axial compression strength for Toray 700 [89, ±0₂, -89] helically wrapped composite tubes as a function of helical angle, θ. These tests were conducted using the multiaxial gripping system. The MY0510 system might be considered to be stronger, but the evidence is not conclusive. A problem with polymer composite materials is that it is impossible to isolate single variables. The viscosity of the epoxy

Table 1. Basic epoxy properties.

Epoxy System	G _m (ksi)	s _{c, flow} (ksi)	t _y	T _g (°C)	Viscosity (P)
DER332-T403	160	12	6.5	90	7.8
Anhydride	180	18	8.7	140	3.4
MY0510-HY350	205	28	10.7	180	14

Figure 8. Normalized axial compression strength for T700 [89, $\pm$ 0, -89] helically wrapped carbon/epoxy tubes with three different matrices.

turned out to be a major factor as well. The MY0510 system has a much higher viscosity than either the Anhydride or DER332 epoxies, which makes it very difficult to process. This resulted in a composite material with higher void contents and resin-rich areas. In contrast, the Anhydride epoxy system produces very high quality composite materials.

A somewhat surprising result was the small variation in compression strength at helical angle between 0° and 10°. Again, processing influences these results; it is very difficult to achieve uniform part quality for helical winding angles less than 10°. Furthermore, helical angles greater than 10° are much faster (cheaper) to fabricate.

Future Work

We have secured a long-term Cooperative Research and Development Agreement with Boeing Commercial Airplane Group to study the "Strength and Durability of Continuous Fiber Polymer Composites." Natural extensions of our past efforts in

"Characterizing the Failure of Composites" will be to modify ORTHO3D to model long-term thermal-viscoelastic effects for these materials. The multiaxial test specimen developed in this program has been selected as a prime test specimen for long-term fatigue testing because of the lack of a free edge associated with the cylindrical test specimen. Finally, we will continue to support the LLNL weapons-related activities in composites, especially in the area of compression optimization, that will make significant use of the multiaxial test specimen.

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Fiber-Optic Raman Spectroscopy for Cure Monitoring of Advanced Polymer Composites

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The curing reaction of an epoxy resin matrix that is used for wet-filament-wound composites was monitored using Raman spectroscopy measured over fiber optics. The resin system consists of the diglycidyl ether of bisphenol-A in combination with a polyethertriamine hardener in a 1:1 stoichiometric ratio. The extent of chemical reaction of the epoxy as a function of time was measurable through changes in peak heights of several vibrational modes. A Raman peak associated with a phenyl ring vibration in the epoxide component was used as an internal reference to correct for density changes and instrumental variations. The feasibility of simultaneous temperature measurements was successfully demonstrated with the same fiber optics used to obtain the cure chemistry data, by measuring the intensity of anti-Stokes Raman scattering from the epoxy.

Introduction

Although significant improvements in the performance of fiber reinforcements and polymer matrix materials have been achieved in the past decade, composite processing technology has not kept pace with these advances. Consequently, high-performance material properties are not realized in composite parts fabricated using current processing methods, and manufacturing costs are high. 'Smart' processing of thermoset matrix composites could dramatically reduce manufacturing costs by reducing the rejection rate and improving part quality, through cure cycle optimization and 'on the fly' process adjustments to account for variations in the chemical composition of the starting materials. Unfortunately, commercially available cure

sensors for automated control are currently limited to dielectric^{1,2,3} or ultrasonic⁴ measurements, which sense only mechanical property changes in the resin and cannot provide a direct measure of the cure chemistry in the composite. Furthermore, recently proposed fiber-optic spectroscopic sensors using mid-infrared^{5,6,7} or ultraviolet-visible^{8,9} wavelengths are either prohibitively expensive and yield little or no additional information when compared with commercially available cure sensors, or contain a large number of spectral interferences that make data interpretation difficult, if not impossible.¹⁰

Raman spectroscopy is an established technique for the analysis of polymers,^{11,12,13} chemical reactions,¹⁴ and thermosetting polymer composite cure reactions.^{15,16} It has many advantages over mid-

Figure 1. Experimental arrangement for dual-fiber probe geometry. Inset emphasizes sample location. M: spectrograph, D: detector, L: lens, S: laser source, FO: fiber optic, F: filter.

infrared absorption and UV-visible fluorescence spectroscopies for polymer composite cure monitoring, including broader applicability, potentially higher sensitivity and selectivity, as well as the freedom from large background corrections caused by fiber absorption. Moreover, Raman spectroscopic measurements can be conducted remotely and *in situ* using rugged, inexpensive, fused silica optical fibers (available from domestic suppliers) and economical, diode laser-excitation sources commonly used in communications and electronic equipment.¹⁷ Subsequent to monitoring the cure reaction of the composite matrix, the quartz optical fibers could be used as embedded strain or damage sensors, or used for monitoring chemical degradation or moisture absorption of the resin.

Progress

During FY-92, the first year of the project, Raman-active vibrational bands in epoxy resins were identified, and tentative band assignments were made for the epoxide functional group and the phenyl ring backbone, from model compound studies. Cure monitoring of standard epoxy resins was demonstrated using several meter lengths of 200- μ m-dia quartz optical fiber using either single-fiber or dual-fiber probes.¹⁸ The single-fiber probe experiments were discontinued due to problems with high fiber background and the inability to accurately correct the data. The utility of economical near-infrared (NIR) diode lasers as excitation

sources for cure monitoring was demonstrated in comparison studies with a conventional Ti-sapphire laser operating at 819-nm wavelength. We also demonstrated for the first time the proportionality between Raman peak ratios and epoxide group concentration in full density epoxide resins, validating the Raman scattering technique for thermoset resin cure monitoring.

Experimental

The epoxy system studied was a 1:1 stoichiometric ratio of diglycidyl ether of bisphenol-A resin (DER 332, Dow Chemical) and a polyoxypropylene triamine hardener (Jeffamine T-403; Texaco Chemical) in a weight ratio of 100/45 resin/hardener. A detailed characterization of this epoxy has been reported elsewhere.^{19,20}

The dual-fiber probe experiment is shown in Fig. 1 and has been described in detail elsewhere.¹⁸ Dual-fiber Raman probes consist of two fibers, side-by-side, cemented in place between two microscope slides so as to meet at an angle of approximately 15°, with the polished probe ends of the fibers extended several millimeters beyond the top slide, as shown in the inset of Fig. 1. One fiber-optic was used to transmit the laser to the epoxy sample, while the other was used to collect the Raman scattering from the sample and transmit it to the detection system. Dual-fiber probe cure measurements were made by thoroughly mixing the liquid epoxy components, and then adding a drop

of the epoxy mixture to the probe tip so as to completely cover the sensor. No effort was made to de-gas the epoxy before injection. Some air bubbles appeared during processing, but these did not appear to affect the signal quality. A cover slide was then placed over the probe area, using spacers to provide a 2-mm gap filled with epoxy, and the entire assembly was placed in a temperature-controlled oven.

Results and Discussion

Separate Raman measurements of the DER 332 resin and Jeffamine T-403 hardener components revealed that the resin component scattering was approximately three to five times as intense as that of the hardener, so that in the 100/45 w/w ratio used for the epoxy cure studies, the resin scattering is dominant. **Figure 2** shows a series of *in situ* spectra obtained during a typical epoxy curing. These spectra are averages of spectra accumulated over several minute intervals. Measurements at one-second intervals yielded comparable results and confirm the potential of this technique for real-time cure monitoring. One major peak near 1112 cm^{-1} remains relatively constant during the curing process and can be used as an internal standard to correct for fluctuations in the sample density, clarity, refractive index, and instrumental factors during measurement. This peak has been associated with an asymmetric breathing vibration of the aromatic rings in the diglycidyl ether of bisphenol-A epoxide resin. Several peaks disappear or shift during the curing process, while several new peaks appear. The most obvious change is in the peak located near 1240 cm^{-1} . This peak loses much of its intensity during the cure and can be assigned to a stretching vibration of the epoxide ring. Although all of the peaks appeared to change

Figure 2. Series of corrected, dual-fiber probe, Raman spectra for the epoxy, taken immediately after mixing (black), 1.2 h at 75°C (gray), and 2.2 h at 75°C followed by a 1-h post-cure at 90°C (white).

Figure 3: Isothermal degree of cure (α) for epoxy at 90°C vs time. Solid and open circles are data from diode-laser and Ti:Sapphire-laser Raman experiments, respectively.

in absolute intensity, probably in response to the changing density of the epoxy as it cures, the ratios of the 1240 cm^{-1} peak to the 1112 cm^{-1} peak decrease smoothly as a function of time.

Figure 3 is a plot of two sets of Raman data for degree of cure, $\alpha(t)$, vs time for an isothermal cure at 90°C . Both experiments used the 2-mm sample thickness, dual-fiber probe arrangement; however, one experiment used a Ti:sapphire laser while the other used a diode laser. The agreement between the duplicate cure experiments is seen to be excellent, indicating a high degree of reliability for the technique. Moreover, the trend of α vs time closely approximates previously published degree-of-cure data for this same DER 332/T-403 epoxy,¹⁹ using NIR absorption spectroscopy¹⁰ at slightly different stoichiometry, temperature, and sample thickness.

In addition to the peak height changes, the peaks were seen to shift to lower energy as the cure progressed. The total shift was small (approximately 5 to 20 cm^{-1}), but was reproducible. A study performed on a previously cured sample showed no change in vibrational frequency with temperature. Consequently, the peak shift to lower energy during cure is not simply a thermal phenomenon, but may be caused by a change in

Figure 4: Anti-Stokes Raman spectrum of the cured epoxy, superimposed on Stokes Raman spectrum for a temperature of 100°C .

the local environment as the curing process occurs. For example, the increase in viscosity during the curing process may stiffen the local environment and mix the vibrations of the individual monomers more strongly with low frequency bulk vibrations. If this is the case, it is conceivable that this phenomenon could be used as a measure of local viscosity, but this possibility has not yet been tested.

The measurement of sample temperature by comparison of Stokes and anti-Stokes Raman scattering (see Fig. 4) is straightforward and readily accomplished. The theoretical ratio of the intensities of the anti-Stokes (I_{AS}) and Stokes (I_S) scattering is

$$\frac{I_{AS}}{I_S} = \left[\frac{\nu(0) + \nu(i)}{\nu(0) - \nu(i)} \right]^4 \exp \left\{ \frac{-hc\nu(i)}{kT} \right\}, \quad (1)$$

where $\nu(0)$ is the laser frequency; $\nu(i)$ is the vibrational energy of the i -th mode; and h , c , and k are Planck's constant, the speed of light, and Boltzmann's constant, respectively. For the epoxy system studies here, a plot of the natural logarithm of I_{AS}/I_S (using the $829 \pm 3 \text{ cm}^{-1}$ vibrational mode) against the inverse temperature, $1/T$, for temperatures ranging from $T = 294$ to 455 K yielded a straight line with a slope of 1200 K , an intercept of 0.517 , and a correlation coefficient of 0.997 . This calibration curve can now be used to determine the *in situ* temperature of the resin system at any given time during a cure cycle. The precision of temperature measurements is limited by the signal-to-noise ratio of the much weaker anti-Stokes peak ($S/N \approx 20$ in Fig. 4). An uncertainty in temperature, $\Delta T \approx \pm 5 \text{ K}$, at 373 K is estimated from the relationship, $\Delta T = T^2/[B(S/N)]$, obtained by differentiation of Eq. 1, where B is the slope of the line. However, the accuracy of temperature measurements can be improved over the results described here, by using high-performance optical filters and also by using longer integration times.

In summary, fiber-optic Raman spectroscopy can be used for remote, *in situ* monitoring of the reaction chemistry and temperature of epoxies used as matrix materials in fiber composites during the cure cycle. While single-fiber probes were found to suffer from fiber-background effects, dual-fiber probes having dimensions on the order of $200 \mu\text{m}$ have been demonstrated successfully. Moreover, the quality of the spectra obtained for the epoxy is sufficient to warrant use of the dual-

fiber Raman probe as an *in situ* quality control technique prior to cure monitoring.

Future Work

Future work will focus on (1) refining and miniaturizing the sensor; (2) evaluating the Raman fiber-optic technique for monitoring other thermoset polymer cure chemistries; (3) performing measurements in thermoset matrix fiber composites; and (4) developing simultaneous, multi-point sampling capability. Based on the preliminary results presented in this paper, we feel that in combination with compact new instrumentation and economical diode-laser excitation sources, fiber-optic Raman spectroscopy can be used to configure a rugged process monitoring and control system for an automated, polymer composite production environment.

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Modeling Superplastic Materials

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We have developed a model that accounts for grain growth during superplastic flow, and its subsequent influence on stress/strain/strain rate behavior. Our studies are experimentally based and have involved two different types of superplastic materials: a quasi-single phase metal, Coronze 638, and a microduplex metal, ultrahigh-carbon steel. We have studied the kinetics of strain-enhanced grain growth in both materials as a function of strain, strain rate, and temperature. An equation for the rate of grain growth has been developed that incorporates the influence of temperature. Our model integrates grain growth laws derived from these studies, with two mechanism-based, rate-dependent constitutive laws to predict the stress/strain/strain rate behavior of materials during superplastic deformation. The material model has been added to the NIKE2D code through an enhancement of the Deformation Mechanism Model. The predictions of the model have been compared with data from several experiments.

Introduction

Superplasticity is the capability to deform crystalline solids in tension to unusually large plastic strains, often well in excess of 1000%. This phenomenon results from the ability of the material to resist localized deformation much the same as hot glass. The material also deforms with very low flow stress. Thus, materials with superplastic properties provide the opportunity to form complex components into shapes very near final dimension. This greatly reduces machining and material costs and minimizes the amount of scrap produced.

Superplastic materials exhibit high elongations, because a deformation mechanism known as grain boundary sliding (GBS) is active. This deformation behavior occurs within a relatively narrow range of temperature and strain rate. If the strain rate is too high, then a different mechanism called diffusion-controlled dislocation creep (slip creep) is activated, and ductilities are substantially reduced. On the other hand, if the strain rate is too low, then a deformation mechanism known as diffusional flow prevails, and the ductility is also reduced relative to GBS. From a commercial standpoint, forming components at high strain rates is attractive, because operations can be done with

less time and cost. Often this means superplastically forming at strain rates close to the slip creep regime. Thus, our work is concentrating on the two higher strain rate regimes, GBS and slip creep.

The active deformation mechanisms also depend strongly on the microstructure of the material, such as an ultra-fine grain structure. Unfortunately, these ultra-fine grains can grow during deformation, resulting in the loss of superplasticity. Thus, it is important to gain a quantitative understanding of this process and its influence on material forming.

For these reasons, material models for the constitutive behavior of materials during superplastic flow should account for microstructure, its evolution, and changes in deformation mechanism throughout the deformation history. The objective of this project is to develop a model of these structural changes and their influence on stress/strain/strain rate behavior, using mechanism-based constitutive laws.

Progress

In our work during FY-91, we (a) established the kinetics of strain-enhanced grain growth for isothermal conditions and (b) developed a model that integrates these grain growth laws with mech-

Figure 1. Microstructure of ultrahigh-carbon steel before deformation (a) and after superplastic deformation to a true strain of .92 (b) and 1.42 (c), respectively. Microstructure consists of ferrite grains and iron carbide particles. Superplastic deformation has caused growth in both the ferrite grains and the carbide particles. The true stress/true strain behavior for this material is shown in (d). Strains at which the photomicrographs were taken are indicated on the plot.

anism-based constitutive equations. During FY-92, we expanded the strain-enhanced grain growth equations to account for the influence of temperature. The material model was also put into the NIKE2D code, and the performance of the model was evaluated with laboratory experiments.

Microstructural Evolution

Our studies have involved two superplastic materials with significantly different microstructures: ultrahigh-carbon steel (UHCS), which has a microduplex structure, and Coronze 638, which is quasi-single phase. In both of these materials, the dominant microstructural change during superplastic deformation is grain growth, and no dynamic recrystallization was expected at the temperatures and strain rates of interest. The UHCS had the composition Fe-1.8C-1.6Al-1.5Cr-.5Mn and had been thermomechanically processed to produce a matrix of ultrafine, equiaxed ferrite grains (mean linear intercept was approximately 0.74 μm)

containing spheroidized carbides. The Coronze 638 (Cu-2.8Al-1.8Si-0.4Co) is a commercially available alloy that consists of essentially pure copper containing a sub-micron-size dispersion of CoSi and CoSi₂ particles. The material was received as a repeatedly rolled and annealed sheet with mean linear intercept grain size equal to 1.9 microns. Further details of the experimental plan are reported elsewhere.¹

Strain-Enhanced Grain Growth. Figure 1 shows the influence of superplastic deformation at 750°C, and a true strain rate of .001/s on the microstructure of UHCS. Figure 1a was taken in the grip section of the sample, and was thus exposed to the testing temperature without plastic deformation. Figures 1b and 1c were taken in the gage section of samples deformed to true strains of 0.92 and 1.42, respectively. A comparison of the figures shows strain-enhanced grain growth in that the ferrite grains have grown. The carbide particles have also coarsened, and the size of the ferrite grains appears to be determined by the intercarbide spac-

Figure 2. Normalized strain-enhanced grain growth vs strain for Coronze superplastically deformed at four true strain rates. Dominant deformation mechanism is noted for each strain rate.

ing. This suggests that the kinetics of grain growth are determined by the kinetics of carbide coarsening. The stress/strain curve in Fig. 1d shows the importance of this grain growth on the deformation behavior of UHCS: increasing the grain size from its initial size ($0.74 \mu\text{m}$) to the size at a strain of 1.42 ($1.48 \mu\text{m}$) has raised the flow stress from 5 ksi to over 9 ksi. Thus, grain growth has produced significant hardening, and the grain size is an important parameter for characterizing the current mechanical state of the material.

In these studies, static annealing grain growth (normal grain growth) and strain-enhanced grain growth are assumed to be additive. Thus, the kinetics of grain growth can be expressed as

$$\frac{\dot{d}}{d_0} = \frac{\dot{d}_a}{d_0} + \frac{\dot{d}_{sc}}{d_0}, \quad (1)$$

where $\dot{d}$ is the total rate of grain growth; $\dot{d}_a$ is the grain growth rate due to static annealing; $\dot{d}_{sc}$ is the grain growth rate due to strain; and d_0 is the initial grain size prior to deformation or exposure to elevated temperature.

The grain structure in the gage section of samples is the result of both static and strain-enhanced grain growth. On the other hand, the grain structure in the grip is the result of static grain growth only. The strain-enhanced grain growth was calculated as the difference in mean-linear-intercept grain size between measurements taken in the gage and grip sections of the sample. We used this procedure to determine the normalized strain-enhanced grain growth response for Coronze. Wilkinson and Caceres² have obtained data for this

Figure 3. Normalized grain growth rate vs strain rate for a number of quasi-single phase and microduplex superplastic materials. Plot is from the work of Caceres and Wilkinson.² Data from our study of Coronze at 550°C, 600°C, and 650°C have been added to the plot. The strain rates over which there is a transition in deformation mechanism from GBS to slip creep, are indicated. The inset shows the three different regions for the curve.

material. The present studies have obtained data at higher strain rates. The strain-enhanced grain growth for Coronze is plotted as a function of true strain in Fig. 2, for tests conducted at 550°C and four strain rates. Results have been normalized by the initial grain size. The tests at the three slowest strain rates were in the region in which GBS is the dominant deformation mechanism. The test at the highest strain rate was in the region where the dominant deformation mechanism was slip creep. For the three slowest strain rates, the normalized strain-enhanced grain growth was found to have a linear dependence on strain and a power-law dependence on strain rate. These results are consistent with the observations of Caceres and Wilkinson on the Coronze alloy.² For the highest strain rate, the grain growth data in Fig. 2 had a much smaller slope. The reason for this will be discussed in the following paragraphs.

Figure 4. Normalized grain growth rate vs strain rate for a number of quasi-single phase and microduplex superplastic materials. Plot is from the work of Caceres and Wilkinson.² Data from our study of the superplastic deformation of UHCS at 750°C has been added to the plot. Strain rate below which GBS is the primary deformation mechanism, is indicated.

The normalized, strain-enhanced grain growth rate (with respect to time) can be calculated from the data in Fig. 2, by multiplying the slopes of individual lines by the strain rate for that test. These grain growth rates have been calculated and added to a figure previously reported by Wilkinson and Caceres,² which shows a log-log plot of normalized grain growth rate vs strain rate. The results are shown in Fig. 3. The plot is quite significant, since it shows data for both quasi-single phase and microduplex materials, for different homologous temperatures and for a range of starting grain sizes. It is clear that a common equation can describe the grain growth behavior of a number of different materials, including Coronze. The curve has three distinct regions. In one region, the nor-

Figure 5. Grain growth rates for Coronze at 450°C, 550°C, and 650°C, predicted by Eq. 5. Calculations are based on the parameters given in Table 1. Experimental data at 550°C and 650°C are given.

Figure 6. Grain growth rates for UHCS at 750°C, predicted by Eq. 5. Calculations are based on the parameters in Table 1. Experimental data is provided.

malized grain growth rate is a power law function of strain rate; at higher or lower strain rates, the normalized grain growth rate reaches a limiting value that is independent of strain rate. These regions are shown schematically in the inset for Fig. 3. The region at the lowest strain rate is the result of static grain growth, whereas the regions at the intermediate and high strain rates represent the result of strain-enhanced grain growth. It is reasonable to assume that the highest grain growth rate represents a limiting rate determined by the kinetics of grain boundary migration. The curve shown in Fig. 3 can be described by

$$\frac{\dot{d}}{d_0} = \frac{\dot{d}_a}{d_0} + \frac{1}{d_0} \left(\frac{\dot{d}_i \dot{d}_u}{\dot{d}_i + \dot{d}_u} \right), \quad (2)$$

where $\dot{d}_i$ is the grain growth rate at intermediate strain rates, and $\dot{d}_u$ is the upper limiting grain growth rate. The intermediate region has a power-law dependence on strain rate, which produces

Figure 7. Calculated grain sizes for Coronze after constant strain rate testing to a true strain of 1 at the indicated strain rates.

the following empirical expression for the normalized rate of grain growth:

$$\frac{\dot{d}}{\dot{d}_0} = \frac{\dot{d}_u}{\dot{d}_0} + \frac{1}{\dot{d}_0} \left(\frac{\lambda_0 \dot{\epsilon}^n \dot{d}_u}{\lambda_0 \dot{\epsilon}^n + \dot{d}_u} \right), \quad (3)$$

where λ_0 and n are constants.

The strain rates at which there is a shift in the operating deformation mechanisms (from GBS to slip creep) are also shown in Fig. 3. It is important to note that the grain growth rates for the three slowest strain rates appear to have a power-law dependence on strain rate. The grain growth rate for the highest strain rate, however, shows a substantially smaller increase with increasing strain rate than the grain growth rates at the lower strain rates. This transition occurs at about the same strain rate as the transition to slip-creep-dominated deformation. The obvious implication is that the loss of GBS as a deformation mechanism has reduced the contributions of strain-enhanced grain growth to the total grain growth rate. Several mechanisms have been proposed to explain strain-enhanced grain growth.³⁻⁶ All of these mechanisms result from grain boundary sliding or grain switching events. It is reasonable to assume that strain-enhanced grain growth will exist only if these mechanisms provide significant contributions to the total strain. Thus, contributions from strain-enhanced grain growth can be limited by a loss of superplastic flow or by the limiting grain growth rates defined by the rates of grain boundary migration.

Identical procedures were used to determine the normalized strain-enhanced grain growth rate for UHCS during superplastic deformation at 750°C. Results are presented in Fig. 4 and fall within the range of grain growth rates for other materials represented on the plot. For UHCS, no upper limit is reached on grain growth rate over the strain rates studied.

Temperature Dependence of Strain-Enhanced Grain Growth. A general extension of Eq. 3 that accounts for the temperature dependence of grain growth can be developed assuming different temperature dependencies for the three processes in Eq. 2. The temperature dependence of normal grain growth kinetics has been studied and equations developed (see, for example, Ref. 7). The primary interest in this study is strain-enhanced grain growth, and thus the intermediate and upper rate

processes represented in Eq. 2. The temperature dependence of these processes can be represented as

$$\dot{d}_i = \lambda_0 \dot{\epsilon}^n \exp \left(\frac{-Q_i}{RT} \right) \quad (4a)$$

$$\dot{d}_u = (\dot{d}_u)_0 \exp \left(\frac{-Q_u}{RT} \right), \quad (4b)$$

where Q_i and Q_u are activation energies for the intermediate and upper regions, respectively; λ_0 and $(\dot{d}_u)_0$ are constants; R is the gas constant, and T is the absolute temperature. Combining these expressions yields a general equation for the temperature dependence of strain-enhanced grain growth:

Figure 9. Stress/strain rate response for UHCS deformed at 750°C.

Figure 10. Hourglass-shaped sample of UHCS deformed at 750 °C for two different extension rates: one in which GBS is the dominant deformation mechanism, and one in which slip creep is the dominant deformation mechanism. The figure shows contours of constant grain size and strain rate for the sample.

Table 1. Parameters used in Eq. 5 for temperature dependence of strain-enhanced grain growth.

	d_0 (μm)	λ_0 [($\mu\text{m/s}$) ⁿ]	$(\dot{d}_u)_0$ ($\mu\text{m/s}$)	n	Q_i	Q_u (kJ/mole)
Coronze	1.9	.178	7.98×10^4	.806	0	104 [*]
UHCS	.74	.156	1.92×10^7	.799	0	170 [†]

* Activation energy for grain boundary diffusion in pure copper⁸

† Activation energy for grain boundary diffusion in pure iron⁹

$$\frac{\dot{d}_{sr}}{d_0} = \frac{1}{d_0} \left\{ \frac{\lambda_0 \dot{\epsilon}^n (\dot{d}_u)_0 \exp \left[\frac{-(Q_i + Q_u)}{RT} \right]}{\lambda_0 \dot{\epsilon}^n \exp \left(\frac{-Q_i}{RT} \right) + (\dot{d}_u)_0 \exp \left(\frac{-Q_u}{RT} \right)} \right\}. \quad (5)$$

The temperature dependence of strain-enhanced grain growth for the Coronze alloy was experimentally evaluated at 600°C and 650°C. The resulting grain growth rates have been added to the plot in Fig. 3, and appear to fall within the range of strain-enhanced grain growth for other materials. These results suggest that strain-enhanced grain growth for the Coronze alloy is independent of temperature and that Q_i for this material is zero. As mentioned in the previous section, the limiting grain growth rate at high strain rate is probably controlled by the rate of grain boundary migration. We therefore assume that a reasonable value for Q_u is the activation energy for grain boundary diffusion. The calculated grain growth rates that are predicted by Eq. 5 are plotted as a function of strain rate in Fig. 5. Calculations are shown for three temperatures, 450°C, 550°C, and 650°C; the parameters are given in Table 1. The calculated grain growth rates show good agreement with rates derived from experimental data. Because the strain-enhanced grain growth is independent of temperature in the intermediate region, at very high temperatures (higher than the temperature studied here), the contribution of static annealing to the total grain growth rate could be significantly higher than the contribution from strain-enhanced grain growth. In Table 1, the parameters for UHCS are also given. Both Coronze and UHCS have very similar strain rate exponents (n) and values for the constant λ . The calculated strain-enhanced grain growth rates for UHCS deformed at 750°C are shown in Fig. 6. Good agreement was obtained with experimental data.

The final grain sizes that would be obtained for Coronze after tensile testing (to a true strain equal to 1) at a constant strain rate are shown in Fig. 7. Calculations, which were done for three temperatures (450°C, 550°C, and 650°C), are based on Eq. 5, using the parameters given in Table 1, and, thus, do not include the effects of static annealing. Results in Fig. 7 show a decreasing final grain size with increasing strain rate and very little grain growth above .1/s for all testing temperatures. Grain growth decreases with increasing strain rate (Fig. 7) despite the increasing grain growth rate

with increasing strain rate (Fig. 5). This occurs because the strain rate exponent (n) in Eq. 5 is less than one. The total amount of grain growth is very sensitive to the value of n .

Mechanical Response

Two rate-dependent constitutive equations have been used for GBS and slip creep,

$$\dot{\epsilon}_{gbs} = A_{gbs} \exp\left(\frac{-Q_{gb}}{RT}\right) \sigma^{n_{gbs}} d^{-p_{gbs}} \quad (6)$$

$$\dot{\epsilon}_{slip} = A_{slip} \exp\left(\frac{-Q_l}{RT}\right) \sigma^{n_{slip}} \lambda^{p_{slip}}, \quad (7)$$

where $\dot{\epsilon}_{gbs}$ and $\dot{\epsilon}_{slip}$ are the strain rates for grain boundary sliding and slip creep, respectively; σ is the stress; A_{gbs} , A_{slip} , n_{gbs} , n_{slip} , p_{gbs} , and p_{slip} are constants; λ is the minimum barrier spacing governing slip creep (typically, the interparticle spacing or the grain size); d is the grain size; Q_{gb} is the activation energy for grain boundary diffusion; and Q_l is the activation energy for lattice diffusion. Since the deformation mechanisms represented by these equations are additive, the total strain rate can be represented by

$$\dot{\epsilon}_{total} = \dot{\epsilon}_{slip} + \dot{\epsilon}_{gbs} \quad (8)$$

The mean, linear, intercept grain size is typically used for the grain size term in Eqs. 6 and 7. For fine grain materials deforming in or near the region of GBS, the minimum barrier spacing is the grain size, and thus for these studies, we have assumed that λ equals d . The grain size was obtained from a time integration of Eq. 1.

Model Implementation and Evaluation

The grain growth kinetics, expressed by Eqs. 1 and 5, and the constitutive laws, expressed by Eqs. 6, 7, and 8, were integrated into an existing material model in the NIKE2D code, called the Deformation Mechanism Model (DMM).¹⁰ This material model solves the constitutive equations, with an implicit solution procedure. The evolution of grain size is also solved with an implicit procedure. The numerical methods used in this model emphasize accuracy, but all of the algorithms are vectorized for the Cray computer. Generally, the

Table 2 Parameters used in Eqs. 6 and 7 for UHCS.

A_{gbs}	Q_{gb}^*	n_{gbs}	p_{gbs}
$[s^{-1}(\text{psi})^{-n}(\mu\text{m})^p]$ 1.84×10^{-3}	(kJ/mole) 177	2.27	3.0
A_{slip}	Q_l^+	n_{slip}	p_{slip}
$[s^{-1}(\text{psi})^{-n}(\mu\text{m})^p]$ 1.41×10^{-21}	(kJ/mole) 252	7.14	3.0
σ in psi d and λ in μm			

* determined experimentally

+ obtained from Ref. 9

speed performance of the DMM is within a factor of three of NIKE2D model 19, a rate-dependent, power-law plasticity model.

We have evaluated the performance of the material model, using a series of experiments of increasing complexity. The first experiments were simple tensile tests conducted at constant true strain rates, and excellent agreement was obtained between model predictions and experimental data. The results were reported in our FY-91¹¹ report. The second set of experiments involved deforming tensile samples through a predetermined strain rate/strain history. This applied strain/strain rate history and the resulting stress/strain response for UHCS deformed at 750°C is shown in Fig. 8. The parameters used in Eqs. 6 and 7 are shown in Table 2. In Fig. 9, we show the stress/strain rate behavior of UHCS. In both cases, excellent agreement was obtained between model predictions and experimental data. A third set of calculations was done to evaluate the material model on a sample containing a non-uniform stress state. The sample had an hourglass shape and was deformed at two different constant extension rates. At one rate, GBS was the dominant deformation mechanism, and at the other rate, slip creep was the dominant deformation mechanism. The extension rates are indicated in Fig. 10, which shows contours of constant grain size (Figs. 10a and 10b) and constant strain rate (Figs. 10c and 10d) after an extension of x in. The sample deformed in the slip creep region has started to neck, and the contours of strain rate are highly localized. The sample deformed in the region of GBS has avoided necking (exhibited characteristics leading to superplastic behavior) by distributing the strain rates throughout the hourglass region.

Conclusions

We draw four conclusions from our work:

1. The dependence of grain growth rate on strain rate for superplastic UHCS and coronze falls on a master curve, as originally proposed by Wilkinson and Caceres.² In the copper alloy, the transition in grain growth rate from a power-law dependence on strain rate to an upper limiting rate occurs at the transition from GBS-dominated behavior to slip-creep-dominated behavior. The transition to an upper limiting rate ($\dot{d}_u$ in Fig. 3) can occur because of a loss of superplastic flow or a limiting grain growth rate defined by grain boundary migration. For UHCS, within the strain rates studied, no upper limit was found to the grain growth rate.
2. An equation describing the temperature dependence of the strain-enhanced grain growth rate has been developed. The equation predicts grain growth rates that agree well with experimental data. For Coronze, strain-enhanced grain growth appears to be independent of temperature in the intermediate region. In the high strain rate region, the strain-enhanced grain growth rate appears to have an activation energy equal to the activation energy for grain boundary diffusion.
3. A material model has been developed that combines the temperature-dependent grain growth law described above and mechanism-based constitutive equations.
4. This model was incorporated into the NIKE2D code, and validation experiments show excellent agreement between model calculations and experimental data.

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