Lawrence Berkeley National Laboratory

Recent Work

Title

Toward New Solders with Improved Fatigue Resistance

Permalink

https://escholarship.org/uc/item/3j23g9gh

Authors

Morris, J.W. Mei, Z.

Publication Date

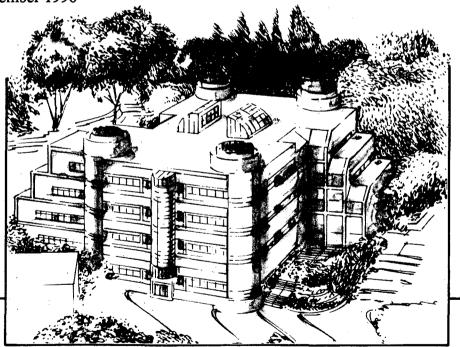
1991

To be published as a chapter in Materials and Mechanics Issues of Solder Alloy Applications, D. Frear et al., Eds., The Metallurgical Society, Publisher, Warrendale, PA, 1991

Toward New Solders with Improved Fatigue Resistance

J.W. Morris, Jr. and Z. Mei

December 1990



Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

Copy a

Bldg.

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

| LOAN COPY |

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Toward New Solders With Improved Fatigue Resistance

J. W. Morris, Jr. and Z. Mei

Center for Advanced Materials

Materials Sciences Division

Lawrence Berkeley Laboratory

University of California

Berkeley, CA 94720

and

Department of Materials Science and Mineral Engineering
University of California

December 1990

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Materials Sciences Division of the U. S. Department of Energy under Contract No. *DE-AC03-76SF00098*.

Toward New Solders with Improved Fatigue Resistance

J. W. Morris, Jr. and Z. Mei Center for Advanced Materials, Lawrence Berkeley Laboratory, and Department of Materials Science, University of California, Berkeley

I. Introduction

It is a challenging task to anticipate those inventions that have not yet been invented. If we were competent to do that we would be too busy filing the relevant patents to write this chapter. What we can discuss is the need for new solders with exceptional fatigue resistance, the essential features of the emerging science of alloy design that can guide the search for them, and the broad outlines of research efforts that may achieve them.

While resistance to thermal fatigue is a critical property of a solder joint, to our knowledge no commercial solder has been specifically developed with this property in mind. There are two principal reasons for this. First, the mechanisms of thermal fatigue in solders have not been understood in sufficient detail to permit alloy development on anything other than a trial-and-error basis. Second, thermal fatigue has been a troublesome, but not critical problem in most microelectronic devices. While solders with improved fatigue resistance would be desirable, they have not been essential.

At this time, however, several parallel trends in microelectronics suggest a need for fatigue-resistant joints. They include the development of surface-mount configurations that require solder joints to bear structural loads, and advances in miniaturization that decrease the potential size of solder joints. Parallel trends suggest the need for new solder compositions, and provide an opportunity to address the issue of reliability in fatigue. These include the development of low-temperature devices and multilevel packages that require solders with very low melting points, and possible legislative restrictions on the Pb content of electronic solders. At the same time, a growing research effort on the behavior of solder joints in thermal fatigue is beginning to generate the fundamental understanding necessary to guide alloy design. There is good reason to believe that the systematic development of fatigue-resistant solders will be a serious activity in many laboratories during the coming years.

The need for new solders with appropriate fatigue resistance has at least three independent sources, which require three rather different solutions.

1. Miniaturization and optimization of advanced electronics. It is almost always possible to "design around" solder fatigue by using leaded contacts or relatively massive solder joints to minimize thermal strain. However, this solution has a price that is paid in device size, performance and manufacturing difficulty. In particular, fatigue-proof designs are often incompatible with surface-mount configurations that optimize size, performance and manufacturability. In the design of microelectronic devices it is desirable to have the

option of shifting more of the burden of reliability from the design to the material. Hence fatigue-resistant solders are needed.

The solders that are most widely used today are Pb-Sn alloys. The most common are near-eutectic compositions (37-40Pb) that combine low melting points, good bonding, manufacturability and familiarity. Where slightly higher melting points are needed, for example, to create soldered components that can be joined without remelting the contacts, the materials of choice have been high-Pb solders such as 95Pb-5Sn or 97Pb-3Sn. Hence the bulk of current research toward fatigue-resistant solders concerns modifications of the Pb-Sn alloys that may offer better fatigue performance while maintaining low cost and manufacturability.

- 2. Complex and temperature-sensitive devices. Increasingly, advanced electronic and photonic devices contain temperature-sensitive components that require the use of solders with very low melting points. Low-melting solders are also required for the manufacture of multilevel packages that utilize sequential layers of solder, each of which must be introduced without remelting its predecessors. The low-melting solders that are currently available have relatively poor mechanical properties. The challenge is to create low-melting solders with fatigue resistance at least comparable to that of the Pb-Sn compounds.
- 3. Legislative restrictions on lead in solder. There is a possibility that the use of lead in electronic solders will be restricted or eliminated by law. This event would create an immediate need for alternative solder compositions with mechanical properties at least comparable to those of the Pb-Sn solders that are in almost universal use today.

To satisfy these needs it is important to begin the systematic development of new solders with improved properties.

II. The Science of Alloy Design

Before considering some of the specific paths that may lead to fatigue-resistant solders it is worthwhile to consider the science of alloy design itself, since we are in the midst of a slow, but inexorable revolution in the way new engineering materials are found. The fundamental change is from development by trial-and-error to invention by alloy design.

A. Background

New engineering materials have traditionally appeared in one of three ways: discovery, in which a new material is encountered by an investigator who is not necessarily looking for it; Edisonian testing, in which the material emerges from screening test on all materials that may conceivably work in a particular application, and Edisonian development, in which the material is found by more or less systematically testing every combination of composition and processing that looks as if it might be promising.

Most of the engineering materials that have come down from the distant past were discovered (including Pb-Sn solders, which were known in biblical times). Cyril Smith [1] argues that most of the common metal alloys were originated by jewelers and artists rather than smiths or founders. Discovery, in the extended sense of fundamental research with no particular engineering goal, continues to be a principle source of new materials with unique properties. Recent examples include superconductors, amorphous metals, and shape memory alloys. However, discovery is no more than an adjunct to materials engineering, precisely because the research is undirected and unpredictable.

Edisonian testing is the principle way in which existing materials find new uses and, in that sense, become new engineering materials. It will remain dominant for two reasons. First, given the cost, difficulty and uncertainty of a materials development effort, managements are usually reluctant to support one until it has been established that existing materials are unsatisfactory. Second, materials needs often become evident only during the design or operation of engineering systems, and often at a sufficiently advanced stage that the engineering schedule for the system precludes the delay involved in a materials development effort. The usual solution is to modify the design or operating schedule to accommodate the properties of the best available materials. But it is not always possible to match available materials to acceptable designs without a serious sacrifice in performance or reliability. Nor is it always wise to gamble that "off-the-shelf" materials can be found to satisfy an increasingly challenging set of future needs. Edisonian testing is complementary to materials development in the sense that its failure to identify adequate or optimal materials defines the problems the materials scientist is asked to address.

Once the need for a new material has been identified, in current practice it is sought in one of two ways, whose superficial similarity obscures a fundamental difference that defines the boundary between Edisonian development and alloy design. In traditional practice (Edisonian development) one systematically varies composition and processing in a search for the desired set of properties. In alloy design one systematically varies composition and properties to obtain a microstructure that imparts the desired set of properties. The distinction between the two approaches is critical. Materials science is incidental to Edisonian development, but is essential to alloy design.

As a review of the relevant technical and patent literature will make clear, Edisonian development remains the dominant approach to new materials, not only in metallurgical industries but in advanced electronics as well. Its operational variables are composition and processing, and it draws on a rich experimental base that addresses the interdependence between composition, processing and properties. Materials science is used, if at all, to rationalize the results. The approach is empirical and suffers from the inherent shortcoming that it is doomed to remain so since there is no explicit mechanistic connection between its input variables (composition and processing) an its output parameters (properties). While useful engineering materials will continue to emerge from research undertaken along these lines, their invention will always involve more art than science.

While we may hope that new fatigue-resistant solders will be discovered, and can be fairly confident that at least some promising new compounds will emerge from

Edisonian development programs that are now underway, the purpose of this chapter is to explore the possible application of systematic alloy design.

B. Alloy Design

As systematic approach to the design of new materials is inherent in the structure of materials science itself. The content of materials science can be expressed in two statements:

The engineering properties of a material are determined by its composition and its current microstructure. The microstructure is determined by the composition and the processing the material has received.

Read backward, these relations become a recipe for alloy design. Given appropriate mechanistic understanding, the set of needed properties is translated into a combination of composition and microstructure that may achieve them. A processing sequence is then chosen to achieve the desired microstructure.

It is possible to identify examples in which something approaching a first-principles approach to alloy design has been successfully applied. Most concern the design of semiconducting or optical materials where the structure-property relations are relatively simple and the relevant microstructural variables are easily characterized and controlled (Von Hippel [2] was talking about what he called "molecular engineering" thirty years ago). It is more difficult to design structural materials whose critical properties include resistance to deformation or failure. The microstructure-property relations are more subtle in this case, the microstructures are more complex and less controllable, and the alloys must ordinarily satisfy a complex set of simultaneous property requirements. (For example, a successful solder must have a low melting point and the ability to bond conductor interfaces, and can be processed only within narrow limits that are largely set by the processing the whole component receives.) For these reasons the successful design of structural alloys is most often accomplished through a more limited approach we shall call the *critical flaw method*.

C. Alloy Design by the Critical-Flaw Method

In the critical-flaw method one confines the alloys of potential interest to a set whose engineering properties are satisfactory with a single exception, the critical flaw (or, at most, a small set of exceptions). One then does research to identify the metallurgical mechanism of the critical flaw in the alloys of interest, hypothesizes a microstructural change that will overcome it, proposes a composition or process modification to achieve that change without disturbing the other necessary engineering properties, and makes and tests samples. If the tests are not successful, as is usually the case, the results are analyzed to determine the mechanism of failure and the process iterated until, hopefully, a successful

result is obtained. It is then usually necessary to fine-tune the alloy to re-establish an appropriate complex of engineering properties.

This is the method that has been used in most of the successful systematic developments of new structural alloys. The critical flaw has ordinarily been low strength, low toughness, or susceptibility to environmental damage.

While the authors know of no example of the systematic design of an alloy for thermal fatigue resistance, the problem of designing superior solders would seem to be amenable to this approach. Systems with satisfactory melting temperature, flow, and bonding characteristics are well known. The problem is to modify them so as to impart superior thermal fatigue resistance without destroying these properties. The problem is, however, made difficult by the uncertainty of the strain-temperature cycles actually experienced by the solder joint, the absence of probative laboratory tests that are agreed to simulate thermal fatigue, and the limited mechanistic understanding of thermal fatigue in solder materials.

III. Pre-Conditions to the Systematic Design of Fatigue-Resistant Solders

A. Constraints on composition and processing

The principle purpose of a solder joint in a microelectronic device is to provide a metallic connection between conductors on different components. To provide an effective bond the solder must spontaneously wet the metallic lands on the components and must do so at sufficiently low temperature that it can be be applied without overheating the semiconducting elements of the device. Since hundreds to thousands of solder contacts are contained in a typical microelectronic device, the manufacturability of the solder joints is also critical. The solder must wet and flow easily so that the joints can be made in continuous operations.

The stringent constraints on the melting temperatures, bonding characteristics and flow properties of solder materials for microelectronic devices severely limit the options available for alloy design, and virtually dictate the use of the "critical flaw" method to design solders with superior fatigue resistance. Only a few basic compositions are suitable; the permissible changes in composition are limited to minor solute additions. Improvements in fatigue resistance must, therefore, be obtained by manipulating the microstructure. However, microstructural modifications are also constrained by the fact that the solder is processed during the manufacture of the device. The processes that are used to control manufacture must be compatible with suitable manufacturing steps.

While the constraints on solder materials are stringent, they are neither completely rigid nor completely known. The solder must have a low melting point and good bonding characteristics, but the additional constraints imposed by manufacturability are less clear. They will ultimately be decided by an economic balance between the advantages in performance and reliability a more fatigue-resistant solder would offer and the costs associated

with a more elaborate, or simply different manufacturing procedure. For example, it is often possible to control the thermal processing of a solder joint, at least in theory, by using laser treatments to reflow the solder under controlled conditions. However, such treatments are potentially very expensive, and would necessarily have to be justified by a dramatic improvement in fatigue life that imparts an equally dramatic improvement in performance. As we shall discuss in more detail below, it may even be possible to achieve a significant improvement in the fatigue life of small joints by simply increasing the cooling rate during joint solidification, but even this change might require a much more stringent processing control than is presently imposed, with costs that are difficult to anticipate.

These considerations suggest the desirability of a systematic study of present and potential ways of manufacturing solder joints with a view toward defining the ranges of properties and process sequences that might be permissible for new solders, to establish boundaries on materials research. In the absence of such guidelines, short-term research toward fatigue-resistant solders may best be confined to compositions and treatments very much like those in current use. It would then seek minor modifications in composition or processing that would lead to improved fatigue resistance in solders that could replace existing grades in existing manufacturing lines or slight modifications of them.

B. The microstructure-property relation

The constraints outlines above suggest that research toward fatigue-resistant solders should employ the critical-flaw method to improve the properties of solders very much like those now in use. To do that we must define the mechanistic sources of inadequate fatigue resistance in existing solders, identify achievable microstructural modifications that would defeat those mechanisms, and quantify the improvement that is achieved so that designers can assess the economic viability of the new materials.

It would be useful if we could simply adopt the results of fundamental studies that reveal the general mechanisms of fatigue fracture in materials. While it is possible to derive some help from this background knowledge, research on other materials is of less value than we might hope. There are several factors that make the solder fatigue problem different. First, solder is used at a high homologous temperature. The upper limit of the thermal cycle in an operating joint approaches the melting point of the material. This has the consequence that, even in the simplest case, the response of the solder to cyclic loads combines creep and fatigue. While the mechanisms of failure by creep and by fatigue are at least moderately well understood, the mechanisms of failure under combined creep and fatigue are a complex combination of the two whose details depend on the precise nature of the material and the load. Second, solder is ordinarily used in an as-cast microstructure. At high homologous temperatures this microstructure is unstable with respect to coarsening, precipitation or reconfiguration, and, hence, may change monotonically as fatigue proceeds or cyclically with each imposed thermal cycle. Third, the solder joint is a composite sandwich in which relatively soft solder joins relatively rigid metal lands, usually with a layer of brittle intermetallic phase at the interface.

Thus the load, homologous temperature, microstructure and composite configuration of the solder joint differ qualitatively from the situations in which fatigue is ordinarily studied. While prior research on the mechanisms of fatigue can provide some useful guidance, they cannot be assumed. The mechanisms of solder fatigue must be specifically identified to provide appropriate guidelines for the design of new solder alloys.

To define the mechanistic sources of thermal fatigue in solder we need probative fatigue tests that simulate the fatigue cycles that are experienced by joints in service. The status of simulation testing is reviewed by Frear [3] in this book. The current status is not entirely satisfactory from the perspective of alloy design. The stress-temperature cycles experienced by solder joints in service are only approximately known, and vary with joint configuration and location in the device in ways that are poorly understood. This situation is likely to persist for some time into the future.

The mechanistic guidelines that are available for alloy design are hence derived almost entirely from laboratory tests that assume simple load configurations, coupled with metallurgical analysis of failed joints that provide some indication of whether the mechanisms observed in the laboratory are also applicable in practice. Most of the pertinent data concerns near-eutectic Pb-Sn solders loaded in shear. Since the dominant fatigue load in many configurations are likely to be in shear, a number of investigators have studied fatigue, thermal fatigue and creep-fatigue under shear conditions. This research is reviewed in the article by Frear [3], and has led to the identification of a dominant failure mechanism in eutectic Pb-Sn solders that can be addressed metallurgically. We shall treat this case in some detail in the following section, since it forms the background for most current research toward fatigue-resistant solder.

Much less is known about the mechanisms of fatigue in non-eutectic Pb-Sn solders, or in solders from other binary systems. Work reviewed elsewhere in the volume (Frear [3], Vaynman, et al. [4]) suggests some relevant failure mechanisms, including normal fatigue through the formation of persistent slip bands and the propagation of cracks, creep-induced cavitation at grain boundaries, and intergranular failure. While these mechanisms are certainly pertinent, the research that identifies them is primarily tension-tension fatigue under isothermal conditions, and their relevance to failure of solder joints remains somewhat unclear.

Since the microstructural mechanisms of shear fatigue in eutectic Pb-Sn solders are reasonably clear it is possible to identify clear directions for the design of modified materials with improved fatigue resistance, and we do so in the following section. Given the uncertainty in the dominant mechanisms of thermal fatigue in other cases it is more difficult to identify promising directions for alloy design, and will remain so until the structure-property relations governing fatigue in these alloys are more fully understood.

IV. Paths to Eutectic Pb-Sn Solders with Exceptional Fatigue Resistance

While the detailed stress-strain path imposed on a solder joint depends on the joint configuration, and is not completely known for any configuration, it is clear that cyclic shear at relatively slow strain rates is critical to most cases of thermal fatigue. The reason is the source of thermal fatigue, which is due to the difference in the thermal expansion coefficients of the materials on the two sides of the joint. Differential thermal expansion causes a relative displacement of the faces of the joint in shear. The specific geometry of the joint and the devices it joins may have the consequence that some regions of the joint experience a mixed stress state, or even a pure tension, rather than a simple shear. However, shear stresses are almost always applied and are clearly the dominant fatigue loads in many common joints.

Since the solder material that is most commonly used in a solder joint is eutectic Pb-Sn solder (63Sn-37Pb), much of the recent research on the mechanisms of fatigue has concentrated on near-eutectic Pb-Sn solders in shear. As discussed by Frear [3] in his companion article, the basic mechanisms of fatigue in this case are reasonably well understood, and have been verified by comparison to the results of fatigue tests on actual components. It is worth summarizing the mechanisms to lay the groundwork for suggestions on how they may be defeated.

A. The Mechanism of Thermal Fatigue in Shear

Microstructure of eutectic solder

When eutectic Pb-Sn solder is solidified in moderate cooling it adopts a characteristic microstructure like that shown in Figure 1, which can be understood in terms of the Pb-Sn phase diagram that is shown in Figure 2. The material solidifies near the eutectic temperature into a classic eutectic microstructure that consists of parallel lamellae of Pb-rich phase in a matrix of Sn. The microstructure is divided into grain-like colonies within each of which the Pb-rich lamellae are nearly parallel. These colonies are the features that are referred to as "grains" in much of the technical literature on solder. In an ideal case they would be grains in the sense that the Sn matrix phase would be a continuous single crystal. In some cases the tin matrix within a colony does appear to form a single grain [5]. In others it does not. Electron microscopic studies [6] show that colonies in eutectic Pb-Sn solder are often not true grains at all; both the Pb- and Sn-rich phases are often subdivided into many individual grains. When the solder is slightly off-eutectic in composition, for example, 60Sn-40Pb, distinct (pro-eutectic) grains of Pb-rich phase also appear.

As the solder is made to solidify at increasingly high cooling rates the microstructure of the solder changes in that the Pb-rich regions of eutectic become more rod-like and closely spaced and the colony size becomes smaller. At very high cooling rates both the Pb-rich and Sn-rich phases may appear in the form of small, equiaxed grains [5,7-8].

The eutectic microstructure of as-solidified solder is unstable because of the very high surface-to-volume ratio of the phases it contains. If the solder is held at room tem-

perature or above the eutectic microstructure coarsens through a continuous, diffusion-controlled process. The coarsening is particularly pronounced near the colony boundaries, where the gains can reconfigure with relative ease. The coarsening process is slow, but continuous, and has the consequence that the appearance and the mechanical properties, such as strength or hardness, change continuously with time after the solder joint is made.

The coarsening process is strongly accelerated if the solder is deformed mechanically. Mechanical deformation triggers recrystallization at room temperature and above. The microstructure changes into an equiaxed mixture of Sn and Pb-rich grains, as illustrated in Figure 3. Recrystallization is followed by grain growth at a rate that increases with temperature. Recrystallization dramatically changes the mechanical properties of the solder [9]. The recrystallized material is much softer than the same material in the eutectic microstructure, and deforms in creep at a very high relative rate. Recrystallized solder is superplastic, while solder in the eutectic microstructure is not.

The interfacial intermetallic layer

The strong adhesion that is established between Pb-Sn solders and conducting pads of copper or nickel is due to a chemical reaction between tin in the solder and copper or nickel in the pad that establishes a thin, adherent intermetallic layer along the interface. The intermetallic layer between a near-eutectic solder and copper is, in fact, a bilayer, as shown in Figure 4. The copper surface is coated by a thin layer of the ε-phase intermetallic, Cu₃Sn, which is separated from the solder by a thicker layer of the η-phase intermetallic, Cu₆Sn₅. The Cu₃Sn intermetallic is extremely brittle, and fractures easily along the grain boundaries of the Cu₃Sn grains when the surface is bent. The Cu₆Sn₅, η-phase, presents a very rough interface to the solder. Grains of Cu₆Sn₅ grow out into the solder in spiky, whisker-like crystals of hexagonal morphology, which reflect the hexagonal crystal structure of the η-phase. The morphology of an interface with 60Sn-40Pb is shown in Figure 5. This intermetallic is also brittle. Grains of Cu₆Sn₅ cleave easily under stress.

Large η -phase precipitates are also found in the bulk of the solder. These have the curious morphology shown in Figure 6; they are long, hexagonal rods that are hollow along their axes and filled with solder. Specific studies [10] show that these intermetallic precipitates form as whiskers on the Cu surface during initial wetting, break off the surface, and redissolve slightly in the liquid solder before solidification to acquire their hollow appearance. Despite their size, these intermetallic precipitates usually have no more than a secondary influence on the mechanical properties of the solder joint.

The basic mechanism of fatigue in shear

Since there are many possible solder joint configurations and several possible microstructures of the solder in solidified joints, it is quite possibly premature to talk about "the" mechanism of thermal fatigue of eutectic solder in shear. Nonetheless, every test of which we are aware in which a eutectic solder joint was deformed to failure in thermal fatigue, isothermal fatigue, or creep at high temperature under predominantly shear loading led to failure by the same basic mechanism. The quantitative measures of fatigue life vary

with the precise experimental conditions and microstructural details. However, so long as the initial microstructure is of the eutectic type and the peak temperature is above room temperature the basic mechanism of failure is the same.

The mechanism is illustrated in Figure 6, which shows the behavior of a 60Sn-40Pb joint as it is cycled from -55°C and 125°C. As the cycling proceeds the shear deformation concentrates into shear bands that are clearly marked because of the apparent coarsening of the microstructure. Figure 7 is a detailed view of a shear band. Fatigue cracks grow through these bands as shown in Figure 8. A review of published cross-sectional micrographs of solder contacts that failed during actual or simulated device operation shows that this fatigue mechanism has been widely observed in near-eutectic solders [11-13].

The mechanism is intimately connected with the evolution of the microstructure and is accelerated by the destructive interference between inhomogeneous shear deformation and microstructure coarsening. Inhomogeneous shear deformation in the solder triggers inhomogeneous coarsening of the eutectic microstructure that is concentrated in the bands of maximum shear. Since the microstructure softens as it coarsens, shear deformation concentrates in the coarsened regions, which therefore coarsen more rapidly. Eventually, cracks form and propagate through the coarsened bands.

The role of the microstructure in thermal fatigue

A closer study of the sequence of microstructural changes that occur during shear failure, whether through thermal fatigue [10], isothermal fatigue above room temperature [14,15] or high temperature creep [16,17], reveals the same sequence of internal changes, which can be described as follows.

The microstructural event that initiates the pattern of failure is the inhomogeneity of plastic deformation of a eutectic microstructure that is deformed in shear. Figure 9 shows the deformation pattern that forms when a near-eutectic solder is deformed slowly in shear at elevated temperature, as revealed by relief at the surface of the specimen. The deformation pattern includes a nearly straight band of deformation that lies parallel to, but slightly displaced from the solder-copper interface together with several irregular deformation bands that lie approximately perpendicular to the interface and cross the solder joint. A metallographic examination of the same surface after a light polish and etch establishes the correspondence between the deformation bands, Figure 9a, and the shear bands of recrystallized material through the microstructure, Figure 9b. Closer inspection shows that the parallel band in Figure 9 crosses eutectic colonies while the perpendicular bands tend to follow colony boundaries. In all cases the parallel deformation band originates at one side of the lateral surface of the solder joint.

The mechanism that initiates the coarsened band seems straightforward. It is well known that the eutectic microstructure in the Pb-Sn system is unstable with respect to recrystallization if it is deformed at a high homologous temperature or exposed to high temperature after deformation. Inhomogeneous shear strain creates a band of concentrated

plastic deformation, which is greatest at the free surface near the stress concentration point. The eutectic recrystallizes there to relieve the accumulated deformation. Since the deformation is local and largely confined to a thin band, only this band of material recrystallizes.

The mechanism of growth of the recrystallized band also seems straightforward. The band grows by the progressive recrystallization of the deformed material. Recrystallization occurs predominantly at the tip of the planar band of previously recrystallized material, and is expected to appear there because this should be the most highly deformed element of material. Since the recrystallized material is soft compared to the eutectic material surrounding it, a narrow band of recrystallized or coarsened material in a eutectic matrix behaves mechanically very much like a narrow crack. Since the applied stress is a simple shear in the plane of the crack the strain field at the crack tip is a mode II deformation zone. The plastic strain field for a mode II crack has been solved for a Von Mises material by McClintock, et al. [18] and is diagrammed in Figure 10. Note that the deformation field is narrow and tends to confine the deformation to the plane of the crack. The next increment of recrystallization near a propagating band of recrystallization that behaves like a mode II crack should occur in the most highly strained material, which lies in the plane of the crack near the crack tip. It follows that the recrystallized band tends to remain plane and narrow while it extends itself along a shear plane, as is observed.

Inhomogeneous shear deformation in the solder triggers inhomogeneous coarsening of the eutectic microstructure that is concentrated in the bands of maximum shear. Since the microstructure softens as it coarsens, shear deformation concentrates in the coarsened regions, which therefore coarsen more rapidly. The preferential coarsening of the Sn grains in the shear bands is pronounced (Figure 11). Eventually, cracks nucleate and propagate through these planar bands.

B. Metallurgical Methods for Defeating the Shear Fatigue Mechanism

Given that the shear fatigue failure of eutectic solder is driven by the formation of recrystallized bands in the plane of shear, the route to improved fatigue resistance is a metallurgical modification that inhibits either the formation of the bands or their propagation through the specimen. One may prevent the formation of recrystallized bands by homogenizing the mechanical response of the specimen so that the shear deformation does not concentrate in inhomogeneous bands. Alternatively, one may prevent the growth of bands by interposing microstructural obstacles that limit their extent.

Three generic metallurgical modifications have been suggested to improve the fatigue resistance of eutectic solders by achieving one of these two effects. First, one can use thermomechanical processing to replace the eutectic microstructure by a fine-grained, equiaxed one. The material should then deform homogeneously; in fact, it should be superplastic at the high homologous temperatures experienced in the solder thermal cycle. The problem is to find a way of accomplishing thermomechanical processing in the creation of the solder joint. Second, one may seek alloying additions that inhibit the formation of the eutectic microstructure and create a more equiaxed pattern. The problem is to identify practical alloying additions that are sufficiently effective at low concentrations to cause a

significant improvement. Third, one may introduce a dispersion of second-phase particles to prevent the growth of recrystallized bands. The problem is to identify a dispersant that can be uniformly distributed through the solder in sufficient density to inhibit the growth of bands without unduly harming the manufacturability of the solder joint (for example, by raising the viscosity of the solder to unacceptable values).

There is active research along each of these lines.

C. Grain Refinement; Superplasticity

It has been known for many years that eutectic Pb-Sn solder can be recrystallized into a fine-grained two-phase mixture that is not only homogeneous in its deformation, but exhibits superplasticity at intermediate strain rates. Superplasticity is marked by a characteristic behavior of the steady-state creep rate at intermediate stress levels.

If a sample of the bulk solder is deformed and held at moderate temperature, the microstructure recrystallizes into the morphology shown in Fig. 3. The resulting steady-state creep rate is drawn schematically in Fig. 12 [19]. The creep rate in shear, $\dot{\gamma}$, is given as a function of the applied shear stress, τ , and temperature, T, by a relation of the generic form

$$\dot{\gamma} = A \tau^n e^{-Q/kT} \tag{2}$$

where A is a pre-exponential factor whose value depends on the microstructure. As illustrated in Fig. 12, the creep rate is divisible into three regimes that represent different deformation mechanisms. At high stress the material creeps by a normal bulk deformation mechanism. The stress exponent is $n \ge 6$, and the activation energy, $Q = Q_D$, is close to that for bulk diffusion. At low stress creep is also dominated by a bulk mechanism ($Q = Q_D$) with n = 3. However, at intermediate stresses the deformation mechanism is qualitatively different. The stress exponent is n = 2, and the activation energy is reduced to $Q = Q_D$, the activation energy for grain boundary diffusion. The deformation is controlled by grain boundary processes, and is superplastic; tensile elongations of several hundred percent are easily achieved. The range of stresses and strain rates for which superplastic deformation is observed varies inversely with the mean grain size; as the grain size is made smaller, the superplastic creep rate increases and the range of superplastic strain rates broadens.

A superplastic microstructure is an attractive possibility for a solder joint. The fine-grained microstructure should deform homogeneously, hence minimizing the formation of inhomogeneous shear bands. Moreover, if the strain rate is held within the superplastic range, the sample exhibits exceptional ductility and should be highly resistant to fatigue. Shine and Fox [20] analyzed the possible effect of superplasticity on solder fatigue life, and concluded that a joint with a reasonable superplastic range should be exceptionally long-lived.

The problem, of course, is to achieve a fine-grained superplastic microstructure in a practical solder joint. The joints are used in as-solidified microstructures that do not normally exhibit superplasticity [16]. However, in specific studies of creep deformation in thin solder joints Shine and Fox [20] found evidence for a superplastic deformation mode. The probable reason was the rapid cooling of the thin joint, which creates a fine microstructure in the as-solidified condition. In support of this interpretation, Rack [21] had observed superplastic deformation in severely quenched eutectic Pb-Sn some years previously, and superplastic creep is often found in as-quenched samples of other eutectic systems, such as Al-Zn [22].

The possibility of achieving superplastic creep in as-solidified solder joints has been pursued in joint research by the authors and M.C. Shine [7,8]. The results show that superplastic creep can be reproducibly obtained in small solder bumps of 2-5 mil thickness. Fig. 13 shows a typical steady-state creep curve for a double-shear specimen like that shown in Fig. 14, containing an array of nine eutectic solder joints of thickness 2-5 mil. Both normal creep ($n \ge 6$) and superplastic regimes ($n \ge 2$) are evident in the creep curve. Studies of the temperature dependence of the creep rate show that the activation energy in the normal creep regime is ≈ 19 kcal/mole, essentially equal to that previously obtained for normal creep in bulk solders, while the activation energy in the superplastic regime is ≈ 12 kcal/mole, very close to that previously measured for superplastic creep [19]. Shear elongations in excess of 100% are easily obtained.

The achievement of a superplastic microstructure appears to involve a combination of rapid cooling and microstructural evolution during the early stages of creep deformation. A typical microstructure of a rapidly solidified solder joint is shown in Fig. 15. It contains both fine-grained volumes and volumes that are more eutectic in structure. However, such joints become uniformly fine-grained after slight deformation, as illustrated in Fig. 16. Apparently the subvolumes of eutectic microstructure are deformed and recrystallized rapidly as the joint is deformed.

The demonstration of superplastic creep in thin solder joints is encouraging, and may offer a major improvement in the fatigue resistance of thin joints. However, the relative fatigue resistance of joints with superplastic microstructures is not yet quantified. Since there is virtually no prior research on the creep-fatigue behavior of superplastic materials, it is difficult to predict the possible benefit. There are also limitations on the potential use of superplasticity in solder joints that ought to be noted. Superplastic creep is confined to a limited range of stresses and strain rates; to obtain its benefits the strain rates of the solder joint during thermal fatigue must be confined to this range. Moreover, superplasticity requires fine grain size, which limits its potential use in any but very thin joints, and raises questions regarding its retention after the grain growth that naturally occurs during an extended service life.

It should be possible to identify minor alloy additions that enhance superplasticity in eutectic Pb-Sn solder by refining the grain size or stabilizing the fine-grained structure against coarsening.

D. Alloy Additions to Suppress Recrystallized Bands

A second metallurgical technique to minimize the formation of recrystallized bands during the fatigue of eutectic Pb-Sn solder is the use of minor alloy additions to promote a more equiaxed microstructure or inhibit recrystallization. A more equiaxed microstructure should provide a more homogeneous deformation pattern and hence minimize the strain concentrations that lead to recrystallized bands. An inhibited recrystallization would prevent the dramatic softening of the inhomogeneous shear bands that happens when they recrystallize, and would hence inhibit the development of these bands.

The only systematic investigation of the influence of common alloy additions that is known to us was a recent study by Tribula [5,23]. She studied the effect of several common alloy additions on the microstructure, creep and thermal fatigue behavior of relatively thick eutectic solder joints. Two additions, In and Cd, were found to have beneficial effects on the creep rate and the thermal fatigue life. In both cases the benefit apparently derives from the influence of the alloy addition on the initial microstructure. Fig. 17 shows the as-solidified microstructures of thick joints of 58Sn-40Pb-2In and 58Sn-40Pb-2Cd joints [23]. In both cases the eutectic colony size is refined with respect to that of a eutectic solder solidified under the same conditions. Moreover, the colonies have diffuse boundaries that contain equiaxed grains of the Pb- and Sn-rich phases.

The creep behavior of the In- and Cd-alloyed solders differs from that of eutectic Pb-Sn in both its morphological and constitutive characteristics. The deformation pattern that develops during the creep of 58Sn-40Pb-2In at moderate stress is shown in Fig. 18. The deformation pattern is much more diffuse than that in the eutectic solder (compare Fig. 9). No well-developed shear bands appear. The steady-state creep rate obeys the generic equation (1):

$$\dot{\gamma} = A \tau^n e^{-Q/kT}$$

Since the joints are relatively thick and coarse-grained the high-stress, bulk deformation mechanism is observed over a wide range of stresses. However, both the stress exponent, n, and activation energy, Q, are substantially decreased by the addition of In or Cd. The stress exponent decreases from 6.0 for 60Sn-40Pb to 3.3 for 58Sn-40Pb-2In and 3.7 for 58Sn-40Pb-2Cd while the activation energy decreases from \approx 20 kcal/mole for 60Sn-40Pb to \approx 16 kcal/mole for 58Sn-40Pb-2Cd. The causes of the changed values of the constitutive parameters is not yet clear.

The In- and Cd-alloyed solders also show improved resistance to thermal fatigue during thermal cycling at relatively high strains. Fig. 19 compares the appearance of 60Sn-40Pb, 58Sn-40Pb-2In, and 58Sn-40Pb-2Cd joints after 3000 thermal cycles at a nominal shear strain of 15%/cycle. The 60Sn-40Pb sample is extensively cracked in a well-developed coarsened band. The In- and Cd-alloyed specimens are uncracked. They coarsen in a much more general pattern, and do not develop an obvious shear band.

The results cited here are preliminary results of a single exploratory investigation. However, they do suggest that alloy additions may prove beneficial in controlling the microstructure, and, hence, the creep and thermal fatigue behavior of even relatively thick solder joints.

E. Second-Phase Dispersants Suppress Growth of Recrystallized Bands

A third metallurgical technique to inhibit the growth of shear bands in the eutectic is to add a dense distribution of second-phase dispersants to the microstructure. The dispersants should interrupt inhomogeneous bands of shear deformation, hence homogenizing the microstructure.

This mechanism is presumably responsible for the increase in the fatigue resistance of Pb-Sn solders as the composition is shifted away from the eutectic value. A number of investigators [24-27] have observed an increase in the fatigue resistance as the composition of Sn-Pb solder is shifted to the Pb-rich side of the eutectic composition. A recent investigation in this laboratory documented the homogenization of fatigue damage at off-eutectic compositions [28]. Fig. 20 compares the surface relief following fatigue for 63Sn-37Pb, 50Sn-50Pb and 40Sn-60Pb joints fatigued isothermally at 75 °C to a strain amplitude of ≈ 10% in shear. The relative dispersion of the strain in the off-eutectic solders is apparent; in the eutectic solder the strain is concentrated in a shear band within which the fatigue crack grows. Fig. 21 shows the same samples after polishing and etching. While shear bands are observed within the eutectic constituent in all three microstructures, the bands are interrupted by the dispersed islands of proeutectic Pb-rich phase in the off-eutectic material, forcing a relatively diffuse overall deformation pattern. The proeutectic Pb-rich phase in the off-eutectic solder is itself liable to fatigue, however, and its internal fatigue is apparently responsible for the observed maximum in the fatigue resistance at intermediate compositions near 50Pb-50Sn.

While the fatigue resistance of Pb-Sn solder improves at off-stoichiometric compositions, these compositions are rarely used in solder joints. The reason is the broad melting range and relatively high upper melting point of the off-eutectic solders, which are undesirable for manufacturing. The Pb-rich solder compositions that have compositions in the range 95-97Pb and solidify into Pb-rich solid solutions at relatively high temperature. These composition remain solid at the melting temperatures of eutectic solder, and are hence useful in multilevel devices. The eutectic constituent in an off-eutectic solder melts at the eutectic temperature, and, hence, cannot be used in multi-level devices that employ eutectic solder in the second stage of manufacture.

It is possible to design solders that contain dispersed second phases, but liquify at the normal eutectic temperature. The approach is to add a dense dispersion of small, inert second phase particles, such as intermetallic or oxide compounds with high melting points. While these remain solid in the liquid phase, and hence affect the viscosity of the solder during reflow, if they do not dissolve in the liquid solder the eutectic liquid melts congruently at the normal eutectic temperature.

Research on dispersion-strengthened solders is currently underway in a number of laboratories, including the U.S. Army Harry Diamond Laboratory, the Aerospace Corporation, and the University of North Texas, among others. While no published reports are available as yet, several investigators have privately reported success in incorporating a reasonably uniform distribution of intermetallic particles into the solder phase.

One interesting example is shown in Fig. 22, taken from recent work at Hewlett Packard. In this case the dispersant is a Au-Sn intermetallic that forms naturally from an Au protective layer on the conductor pad that is wet by the solder. The flow-line pattern of the intermetallic shows a reconfiguration that occurred during vibration testing.

The influence of intermetallic dispersants on thermal fatigue is not yet clear. The proeutectic islands that inhibit fatigue damage in off-eutectic solders are relatively large inclusions. It seems unlikely that intermetallic dispersants of comparable size could be added to the solder without compromising manufacturability. However, it is not certain that dispersants of finer size can successfully prevent the formation of shear bands. Relevant data should appear in the very near future.

F. Design for Fatigue Resistance under Tensile Load

The cyclic load on solder joints of complex geometry often includes a significant tensile component. The mechanisms of thermal fatigue of eutectic solder joints in tension was investigated by Frear, et al. [29]. It differs in significant details from the mechanism of fatigue in shear. Well-defined shear bands did not form in joints loaded in tension. The eutectic microstructure coarsened in a more general pattern. Fatigue crack nucleation concentrated at the interface between the solder and intermetallic, or within the intermetallic itself.

These limited results suggest that the integrity of the intermetallic layer at the solder-substrate interface is a particularly important factor in solder joints subject to fatigue in tension. The integrity of the intermetallic layer is primarily a manufacturing issue. Flaws are introduced at the intermetallic layer principally by lack of wetting at either the solder-substrate or solder-intermetallic interface. Major causes of non-wetting at the solder-substrate interface include non-wettable inclusions in the substrate that penetrate its surface and oxide or contaminant layers that are not fully removed by cleaning prior to soldering. Flaws at the solder-intermetallic interface are particularly likely in pre-tinned components that are aged prior to soldering. Pores in the pre-tinning layer or reconfigurations of the thin solder coat during shelf aging can expose and oxidize the intermetallic surface so that it is not wet by the solder during reflow.

Flaws in the intermetallic layer can also induce early fatigue failure in solder joints. Failures within the intermetallic have been specifically observed in laboratory tests of joints that were given long reflow treatments [6], causing the development of unusually thick intermetallic coatings.

G. Other Eutectic Solders

Eutectic solders from other alloy systems are increasingly of interest because of the increasing need for low-melting solders and the potential need for Pb-free compositions. However, there has been very little prior research on the mechanisms of fatigue in these systems. Recent work in Japan [30] suggests that the Sn-Ag eutectic may have particularly good fatigue resistance, but the mechanisms of failure are not clear. There is relevant current research in several laboratories, including our own.

V. Methods of Imparting Fatigue Resistance to Single-Phase Solders

A. Research status

While nominally single-phase solders, such as 95Pb-5Sn and 97Pb-3Sn, are widely used in electronics, there has been relatively little research into the mechanisms of fatigue in shear (see, for example, the review by Frear [3] that appears in this volume). The available data do show the development of inhomogeneous shear bands in these materials, and the tendency for fatigue cracks to follow these bands. At low strain amplitudes fatigue cracks tend to propagate along grain boundaries, a phenomenon that is observed in both shear and tension-tension fatigue tests.

The thermal fatigue of Pb-rich solders, particularly 95Pb-5Sn, is complicated by the cyclic reprecipitation of the Sn-rich phase. The solubility of Sn in Pb increases strongly with temperature near room temperature. If a Sn-rich phase precipitates, as it does in 95Pb-5Sn, then the phase dissolves and re-precipitates during thermal cycles. This behavior almost certainly influences the progression of thermal fatigue, but, to our knowledge, has not been studied in detail.

Perhaps the most pertinent consistent observation on the mechanism of fatigue in high-Pb solders is the prevalence of an intergranular crack path along the boundaries of the Pb-rich grains. Intergranular fracture has been found in fatigue teats in both tensile and shear loading, in both isothermal and thermal fatigue at temperature ranging from room temperature to 150 °C, at both high and low cycling frequencies, and at both high and low strain ranges. However, there are differences in the details of the fatigue mechanism.

Intergranular failure in the thermal fatigue of 95Pb-5Sn joints is documented in refs. [6,31-32]. In refs. [6,31] solder joints were cycled between -55 °C and 125 °C to provide a nominal thermal strain of 19%. Extensive cracking was observed both parallel and perpendicular to the direction of shear. The cracks had a mosaic pattern, indicating that they propagated along planes of maximum shear, but were observed to follow the boundaries of Pb-rich grains. A similar cracking pattern was observed in isothermal fatigue at large strains [32].

In monolithic specimens of 96.5Pb-3.5Sn in isothermal, tensile fatigue at smaller strains the failure pattern changes with the strain range [33-36]. At high total strains (>

0.3%) fatigue cracks propagate in a mixed transgranular and intergranular mode along grain boundaries and transgranular slip bands. At lower total strains (<0.3%) the failure is intergranular. Intergranular fracture is also promoted by decreasing the cycle frequency [33-36], adding a tensile hold time during the cycle [33-36] or raising the temperature [37]. The intergranular failure mode leads to a decease in the fatigue life, as reflected, for example, in a Coffin-Manson plot [33-36].

The mechanism of intergranular fracture in tension-tension fatigue appears to be the formation and growth of cavities at the grain boundaries. Grain boundary voids have been specifically observed in 98Pb-2Sn solder fatigued in reverse bending [38]. The void density increases parabolically with the number of fatigue cycles in reverse bending, and the voids coalesce to form intergranular cracks. Studies of deformation at the sample surface during the tension-tension fatigue of this alloy suggest that voids nucleate at slip band intersections with grain boundaries and at serrations and nodes in the boundaries that become stress concentration points during grain boundary sliding [39,40]. When the strain range is low grain boundary sliding accommodates the deformation instead of introducing cavities, and voids nucleate at nodes and pinned boundaries. The extent to which these mechanisms apply to the more relevant case of thermal fatigue in shear is not yet clear.

In addition to these specific studies of high-Pb solders, there is, of course, a vast literature on the mechanisms of fatigue in conventional alloy systems. While there may be a wealth of useful ideas in this background material, it is not clear at this time what part of it is relevant to the design of fatigue-resistant solders. Solder fatigue develops through a combination of creep and cyclic plastic deformation, primarily in shear, that is driven by a temperature cycle. Very little of the available data addresses this case.

Both 98Pb-2Sn [41] and 95Pb-5Sn [28] have been observed to recrystallize during fatigue. However, the implications of recrystallization for the fatigue life are not yet clear.

B. Suggestions for alloy design

The identification of a detailed alloy design approach for non-eutectic solders must be deferred until there is more specific information on the relevant fatigue mechanisms. However, the most common applications of the 95-97Pb solders in current devices are in chip-to-chip holder or chip-to-package contacts in computers, where the relatively high melting point of the solder is needed to prevent melting during subsequent processing, and in automotive electronics, where the high melting point prevents melting during service in proximity to the engine. In both these cases the solders experience rather small thermal strains, and, therefore, operate in the regime where intergranular crack propagation has been identified as an important failure mechanism. It would appear that future research might profitably concentrate on the sources and prevention of intergranular failure.

There are three potential sources of intergranular cracking that may be addressed. First, the grain boundaries may be weakened by contaminants. While specific studies [39] suggest that Sn does not accumulate at Pb-rich grain boundaries, other contaminants, such as oxygen, are possible. Contaminants may embrittle the boundaries, or they may harden

the boundaries, inhibiting the transmission of stress from grain to grain. If contamination is present, the grain boundaries can be strengthened by purifying the alloy or gettering contaminants into relatively innocuous precipitates. It is also possible that the grain boundaries are inherently brittle due to relatively poor adhesion from grain to grain. If this is the problem then one may introduce species that promote adhesion, as B and C are known to do in ferrous alloys and Ni-based intermetallics.

Some of the work done to date suggests that the problem is not grain boundary adhesion, but grain boundary sliding that creates local stress concentrations. This problem is exaggerated by large grain size, which facilitates local serration of the boundaries and creates large stress concentrations at grain junctions. Microstructural modifications that achieve a fine, stable grain size would minimize this problem. Fine grain size can be obtained by rapid solidification. However, the stabilization of a fine grain size during fatigue at high temperature requires some pinning mechanism, usually provided by a distribution of precipitates. The Sn-rich precipitates that form on cooling 95Pb-5Sn might be useful at low temperatures [41], but dissolve at temperatures above 100 °C. Hence a third specie should be added to provide a thermally stable precipitate. One possibility is the addition of Cu to form a dispersion of Cu-Sn intermetallics in the bulk. However, Rathore [37] found that the addition of 0.1-0.5% Cu to 95Pb-5Sn decreased the fatigue life by \approx 50%. Further research is needed.

VI. Implications and Suggestions for Future Work

As the encouraging preliminary results of alloy design studies on eutectic Pb-Sn solder suggest, it should be possible to improve the thermal fatigue resistance of solders while retaining the other material properties that are needed for manufacturability and service. The information that is required to do this is a clear understanding of the microstructural mechanisms of fatigue failure under the load and temperature cycles that are experienced by the joint in service. This mechanistic understanding is available for eutectic Pb-Sn solders, at least at a level that permits a serious effort to improve their properties. A similar level of mechanistic understanding is needed for the other solder compositions of interest, particularly including the high-Pb solders, low-melting solders and Pb-free solders.

Many of the research needs that were identified in other chapters of this book are also important to the alloy design effort. In particular, we need improved analytic and experimental results on the loads imposed on solder joints in service, and more probative tests and analyses to predict the life of solder joints in service.

Analytic and experimental data on the imposed loads are needed to refine our understanding of the fatigue environment the joint must survive. Most of the current alloy design studies assume a dominant shear load. While this assumption is supported by postmortem examinations of failed joints, which seem to show the same mechanisms of failure observed in laboratory tests in shear, the rate of fatigue may be significantly affected by the more complex load states experienced in actual joints. In fact, there may be important joint

geometries in which the shear failure modes do not dominate at all. It is important to have this information.

The development of predictive analyses and tests for solder life is important to verify and quantify the improvements in fatigue life that modified solders may achieve. The new alloys that are contemplated in current research inevitably involve some complexity in the composition or processing of the joint, and hence will inevitably add some cost. The hope is that the increased cost will be justified by improved service life, reliability or performance. Such decisions are difficult to make in the absence of a believable, quantitative measure of the degree of improvement.

Finally, future research should identify and address the potential issues of reliability that have not been considered in work done to date. These include, for example, environmental contributions to thermal fatigue, and the consequences of aging during storage or service. While many solder joints are hermetically sealed from the environment, many others are exposed to air or water vapor, and are thus liable to corrosion. It has been suggested [43] that intergranular corrosion is partly responsible for the intergranular fatigue pattern observed in high-Pb solders cycled at small strain amplitudes. This issue needs to be clarified and quantified. While many solder joints are introduced into service almost immediately after manufacture, others are stored for long periods of time. The microstructure of the solder coarsens during periods of storage, and important microstructural features such as the fine grain size that imparts superplasticity may be lost. The microstructure is also expected to evolve during periods of high-temperature exposure in service as, for example, when a device is kept in continuous operation for long periods of time. The associated microstructural changes and their consequences need to be understood before the potential benefit of new solder concepts can be predicted with confidence.

Acknowledgement

The authors are grateful to M.C. Shine and his associates, DEC; D. Frear and W. Jones, Sandia; K. Kinsman, Intel; J. Glazer, Hewlett Packard; W. Winterbottom and his associates, Ford Motor Company; G. Lucey, U.S. Army Harry Diamond Laboratories; and D. Grivas, D. Tribula, T. Summers, A. Sunwoo, H. Hiyashigatani and J. Freer, LBL, for helpful discussions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, U. S. Department of Energy, under Contract No. DE-AC03-76SF00098. Portions of the work reported were supported by the Digital Equipment Corporation under contract to the University of California, Berkeley.

- 1. C.S. Smith, A History of Metallography, University of Chicago Press, Chicago (1960)
- 2. A.R. Von Hippel, *Molecular Science and Engineering*, J. Wiley, New York (1959)
- 3. D.R. Frear, this volume
- 4. S. Vaynman, et al., this volume
- 5. D. Tribula, PhD Thesis, Univ. of California, Berkeley (1990)
- 6. D.R. Frear, PhD Thesis, Univ. of California, Berkeley (1987)
- 7. Z. Mei, D. Grivas, M.C. Shine and J.W. Morris, Jr., <u>Journal of Electronic Materials</u>, in press
- 8. Z. Mei, R. Hansen, M.C. Shine and J.W. Morris, Jr., 1990 ASME Winter Annual Meeting, Dallas, Texas

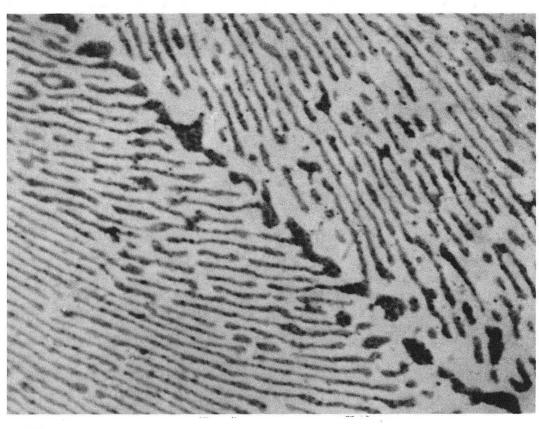
4 33

14 1 167 21 186

- 9. D. Grivas, PhD Thesis, Univ. of California, Berkeley (1978)
- 10. D.R. Frear, D. Grivas and J.W. Morris, Jr., <u>Journal of Electronic Materials</u>, <u>16</u>, 181 (1987)
- 11. H.N. Keller, <u>IEEE Transactions on Components</u>, <u>Hybrids</u>, and <u>Manufacturing</u> <u>Technology</u>, <u>4</u>, 132 (1986)
- 12. J.T. Lynch, M.R. Ford and A. Boetti, <u>IEEE Transactions on Components</u>, <u>Hybrids</u>, and <u>Manufacturing Technology</u>, 6, 237 (1983)
- 13. R.N. Wild, Welding Journal (Res. Suppl.), 51, 521 (1972)
- 14. D. Frear, D. Grivas, M. McCormack, D. Tribula, J.W. Morris, Jr., in *Effect of Load and Thermal History on Mech. Behavior*, TMS-AIME (1987), p. 113.
- 15. D.R. Frear, D. Grivas and J.W. Morris, Jr., in *Proc.*, 3rd Electronic Packaging and Corrosion in Microelectronics Conf., 1987, p. 269
- 16. D. Tribula, D. Grivas, D.R. Frear and J.W. Morris, Jr., ASME Journal of Electronic Packaging, 111, 83 (1989)
- 17. D. Tribula, D. Grivas, D. Frear and J.W. Morris, Jr., Weld. Res. Sup. Weld. J., October 1989, p. 404-s
- 18. F.A. McClintock and G.R. Irwin, <u>ASTM STP 381</u>, American Society for Testing and Materials, Philadelphia, 1984, p. 84; D. Broek, *Elementary Engineering Fracture Mechanics*, Martinus Nijhoff, Amsterdam, 1983, p. 99
- 19. D. Grivas, K.L. Murty, and J.W. Morris, Jr., Acta Met., 27, 731 (1979)

- 20. M.C. Shine and L. R. Fox, <u>ASTM STP 942</u>, American Society for Testing and Materials, Philadelphia, 1988, p. 588
- 21. H. J. Rack and J. K. Maurin, <u>Journal of Testing and Evaluation</u>, <u>JTEVA</u>, <u>2</u>, 351 (1974)
- 22. T.H. Alden and H.W. Schadler, <u>Transactions of the Metallurgical Society of AIME</u>, 242, 825 (1968)
- 23. D. Tribula and J.W. Morris, Jr., <u>ASME Journal of Electronic Packaging</u>, <u>112</u>, 87 (1990)
- 24. E. R. Bangs and R. E. Beal, Weld. Res. Sup. Weld. J., 54, 377s (1978)
- 25. H. Inoue, Y. Kurihara, and H. Hachino, <u>IEEE Transactions on Components</u>, <u>Hybrids</u>, and <u>Manufacturing Technology</u>, 9, 190 (1986)
- 26. D. M. Jarboe, *Thermal Fatigue Evaluation of Solder Alloys*, Technical Communications Bendix, Kansas City: BDX-613-2314, 1980
- 27. R. N. Wild, Some Fatigue Properties of Solders and Solder Joints, 1975, IBM Technical Paper No. 74Z000481.
- 28. T. S. E. Summers and J. W. Morris, Jr., <u>ASME Journal of Electronic Packaging</u>, 112, 94 (1990)
- 29. D.R. Frear, D. Grivas, and J.W. Morris, Jr., <u>Journal of Electronic Materials</u>, <u>18</u>, 671 (1989)
- 30. M. Harada and R. Satoh, 1990, Production Engineering Research Laboratory, Hitachi, Ltd, 292 Yoshida-cho, Totsuka-ku, Yokohama 244, Japan
- 31. D. R. Frear, Grivas and Morris, <u>J. Metals</u>, <u>40</u>, 19 (1988)
- 32. E. Levine, and J. Ordenez, <u>IEEE Trans. Components</u>, <u>Hybrids</u>, and <u>Manufacturing</u> <u>Tech.</u>, <u>4</u>, 515 (1981).
- 33. S. Vaynman, M.E. fine, and D.A. Jeannotte, Metall. Trans. A, 19A, 1051 (1988)
- 34. S. Vaynman, <u>IEEE Trans. Hybrids and Manufacturing Technology</u>, 12, 469 (1989)
- 35. S. Vaynman, and M.E. Fine, in *Proc. 37th Electronic Component Conf. (IEEE)*, p.598.
- 36. S. Vaynman, M.E. Fine, and D.A. Jeannotte, in *Effect of Load and Thermal History on Mech. Behavior*, TMS-AIME (1987), p. 127.
- 37. H.S. Rathore, R.C. Yih, and A.R. Edenfeld, <u>J. of Testing and Evaluation</u>, <u>JTEVA</u>, <u>1</u>, 170 (1973)

- 38. P.J. Greenwood, T.C. Reiley, V. Raman, and J.K. Tien, Scripta Metall., 22, 1465 (1988)
- 39. V. Raman and T.C. Reiley, Metall. Trans. A, 19A, 1533 (1988)
- 40. G.J. Stone and V. Raman, Metall. Trans. A, 19A, 2355 (1988)
- 41. V. Raman and T.C. Reiley, Scripta Metall., 20, 1343 (1986)
- 42. R. Berriche, S. Vaynman, M.E. Fine, and D.A. Jeannotte, in *Proc. of ASM's Third Conference on Electronic Packaging: Materials and Processed & Corrosion in Microelectronics*, M. E. Nicholson, ed., ASM INTERNATIONAL, 1987, p. 169.



10 μm XBB 907-5492

Fig. 1. Optical micrograph of a eutectic Sn-Pb solder, showing colonies and colony boundary.

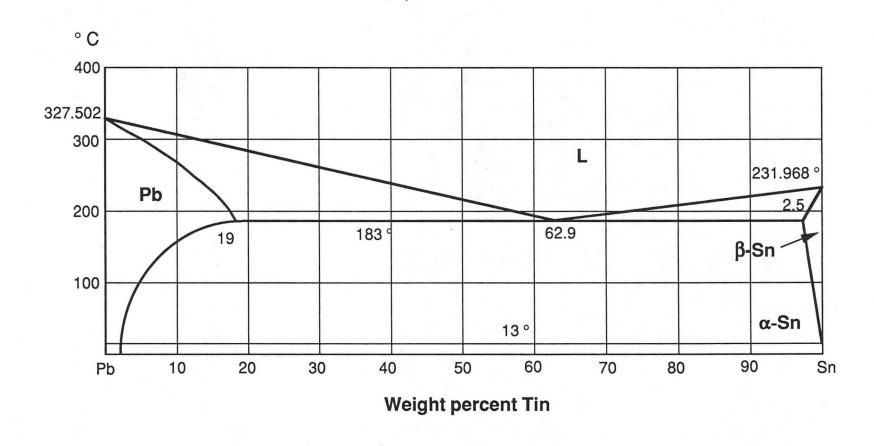
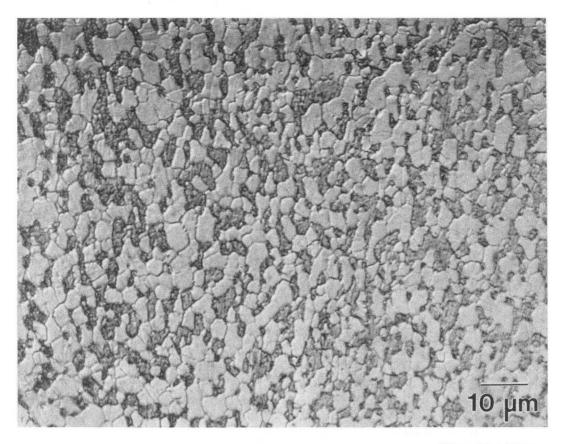
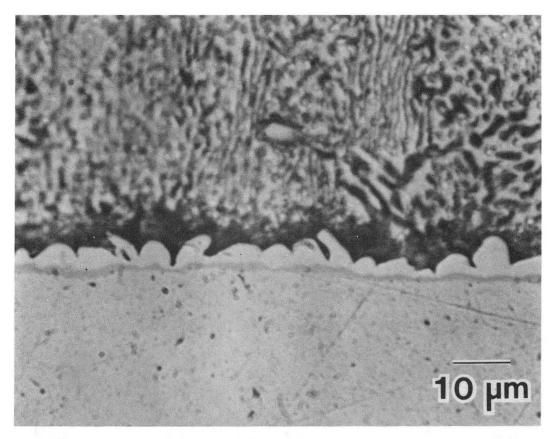


fig. 2. Sn-Pb phase diagram.



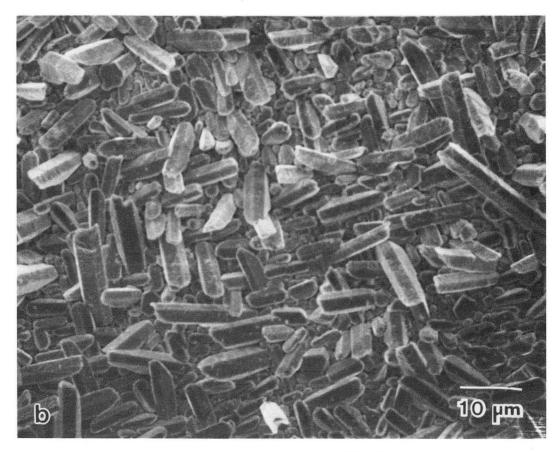
XBB 885-5304

Fig. 3. Optical micrograph showing a worked and annealed 60Sn-40Pb microstructure. The thermomechanical treatment results in a recrystallized microstructure consisting of equiaxed Pbrich and Sn-rich grains.



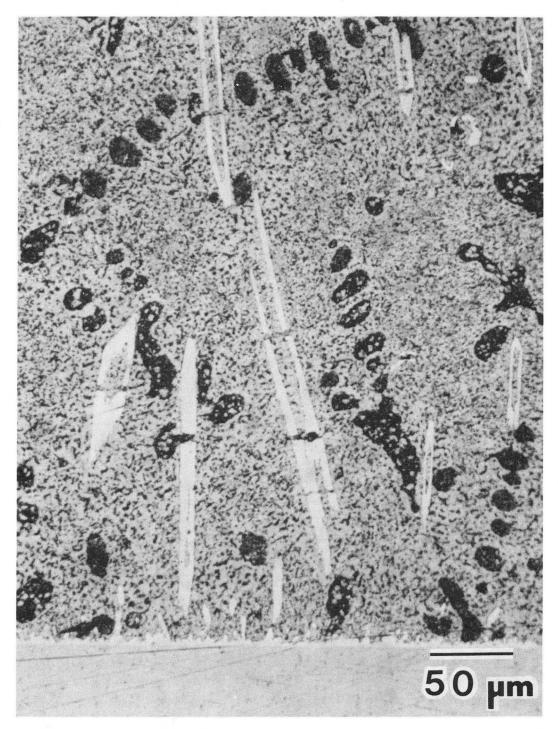
XBB 871-439

Fig. 4. Optical micrograph of a 60Sn-40Pb solder joint on copper, showing a double layer intermetallics at the interface, the ε -phase (Cu₃Sn) is a thin layer coated on the copper, and the η -phase (Cu₆Sn₅) forms a thick and spiky layer.



XBB 876-4404 (Bottom Image)

Fig. 5. SEM micrograph of a 60Sn-40Pb/Cu interface. The solder has been etched away to reveal the spiky, whisker features of the Cu₆Sn₅ intermetallic.



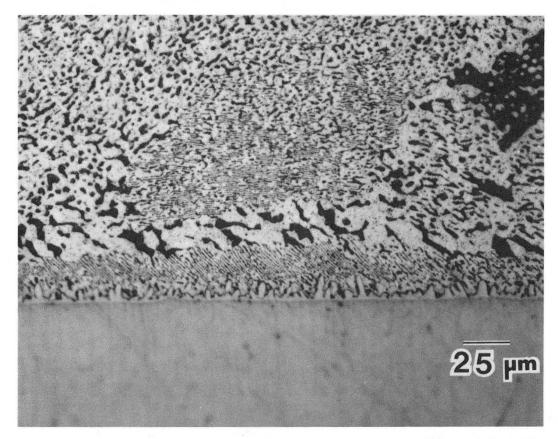
XBB 871-422

Fig. 6. Optical micrograph of Cu_6Sn_5 rods present in the bulk of a 60Sn-40Pb solder / Cu joint.

60Sr-40Pb Thermal Cycle: -55°C

+125°C

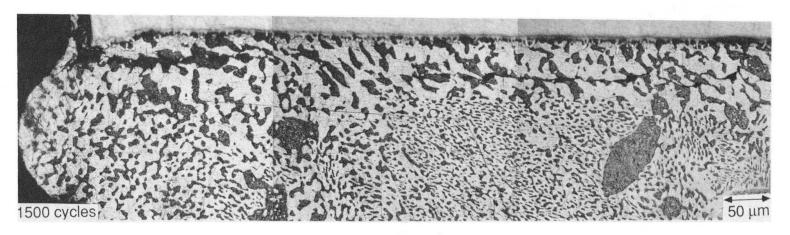
Fig. 7. A series of optical micrographs showing the evolution of a coarsened microstructure within the solder joint as a function of thermal cycles.



XBB 869-7138

Fig. 8. Optical micrograph showing a detailed view of the microstructure within the coarsened band.

60Sn-40Pb Thermal Cycle: 35°C ←→125°C





XBB 872-1247

Fig. 9. Optical micrograph showing a fatigue crack growing primarily along the Sn-Sn grain boundaries.

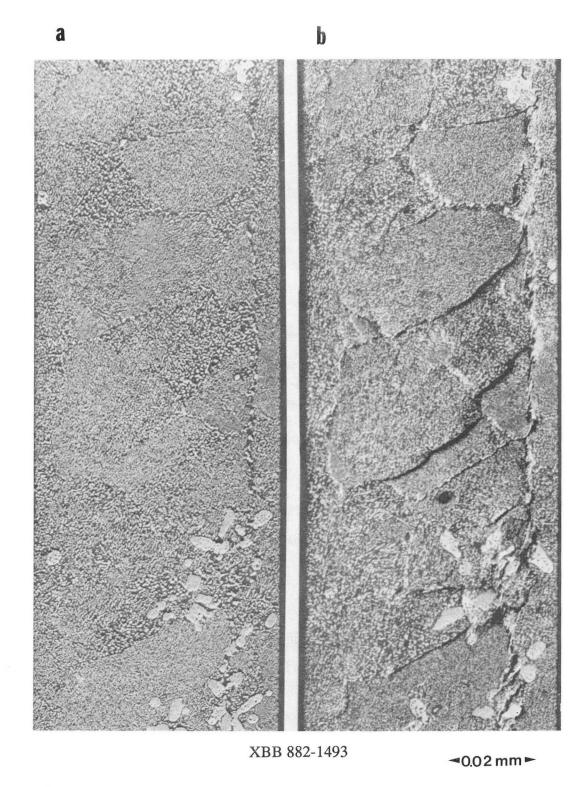


Fig. 10. Optical micrographs of a solder joint deformed in creep. On the right, (b), is the deformation pattern that develops on the surface of the joint as it is slowly deformed; on the left, (a), is the same joint after a light polish. Note the correspondence between the deformation pattern and the location of the bands.

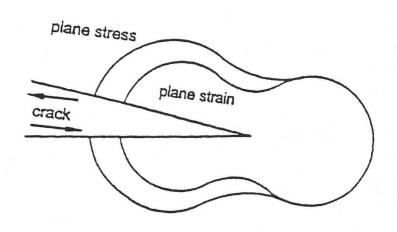
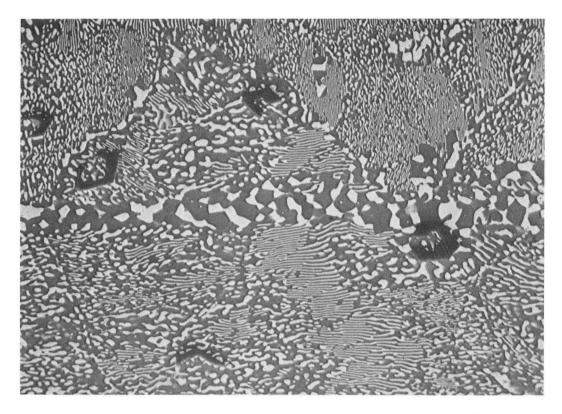


Fig. 11. The plastic strain field for a mode II crack.



XBB 881-277

Fig. 12. SEM micrograph of a solder joint deformed in creep showing a well developed coarsened band.

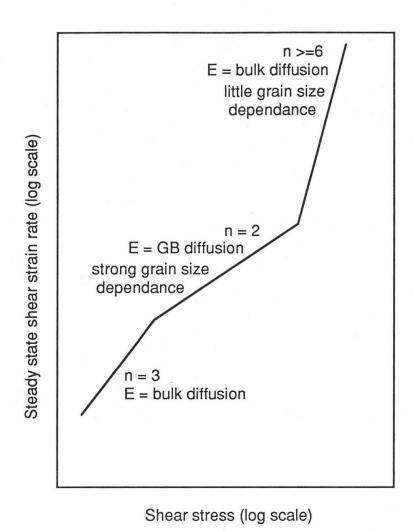


Fig. 13. Schematic plot of creep strain rate vs. shear stress for eutectic Sn-Pb superplastic solder, showing the dependance of the stress exponent, n, and the activation energy, E, on the stress and strain rate.

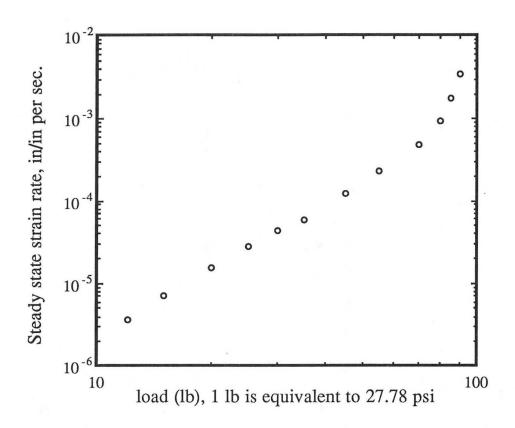


Fig. 14. Steady state shear strain rate vs. shear stress data of a stepped load creep test at 25° C for an air-cooled 60Sn-40Pb solder joint.

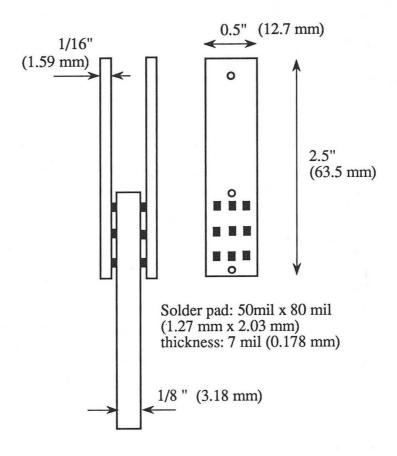


Fig. 15: Double shear creep test specimen.

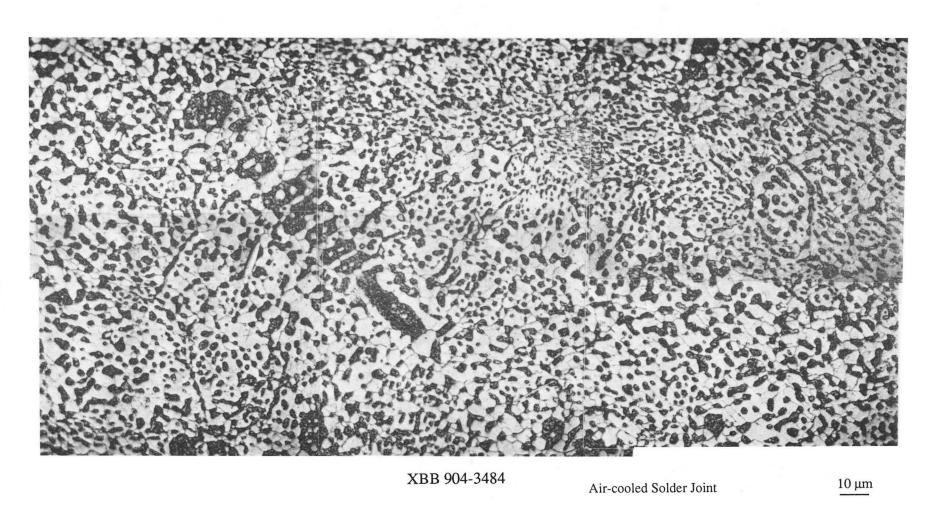
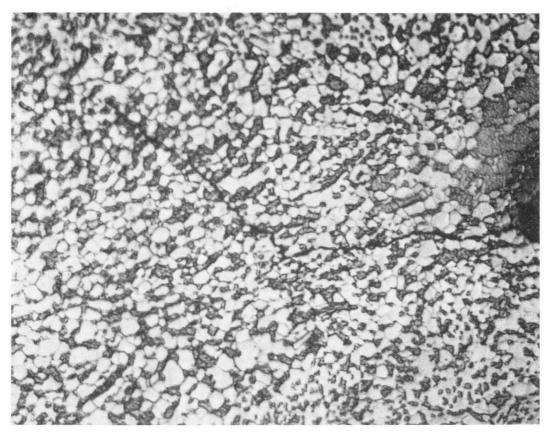


Fig. 16. Optical micrograph of an air-cooled solder joint before creep test. The sample was etched for 20 seconds with a solution of 25 ml H₂O, 5 ml 37% HCl, and 5 g of NH₄NO₃.



XBB 904-3485

65° C, 35 lb (972 psi), LBL16.dat

 $10\ \mu m$

Fig. 17. Optical micrograph of a solder joint after a creep test, showing a crack along Sn-Sn and Sn-Pb grain boundaries. The sample was etched as described in figure 16.

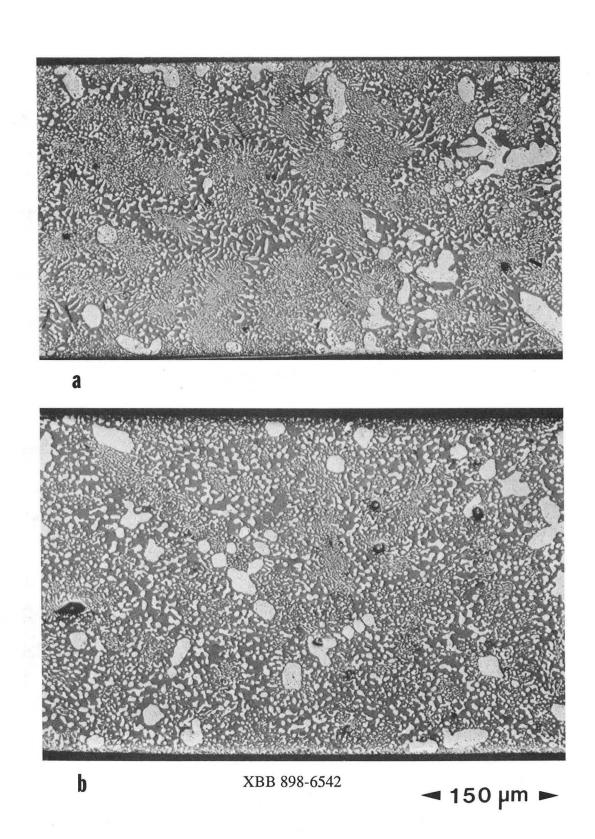
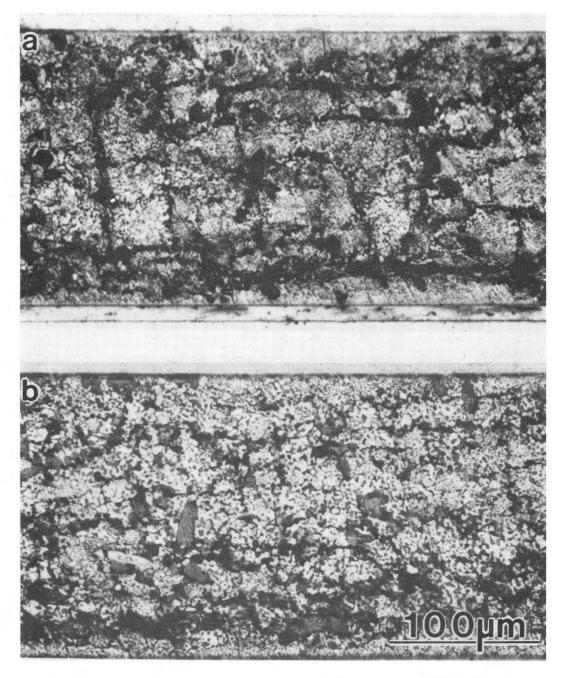


Fig. 18. Optical micrographs of (a) Cd and (b) In alloyed solder joints.



XBB 898-6541A

Fig. 19. The surface relief observed after creep deformation of the (top) Cd and (bottom) In alloyed solders. The deformation patterns reveal uniform deformation occurring throughout the entirety of the joint.

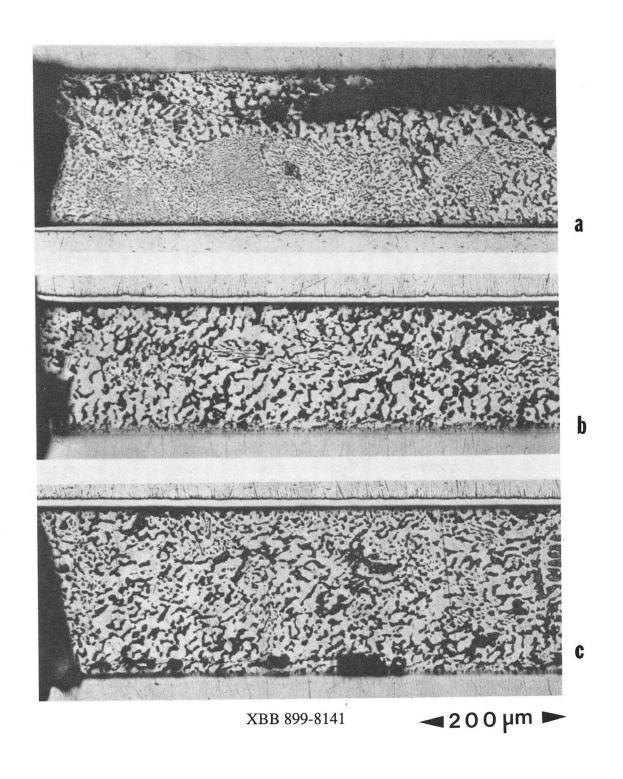


Fig. 20. Optical micrographs (a) 60Sn-40Pb, (b) 58Sn-40Pb-2In, and (c) 58Sn-40Pb-2Cd joints after 3000 thermal cycles at a nominal shear strain of 15% / cycle.

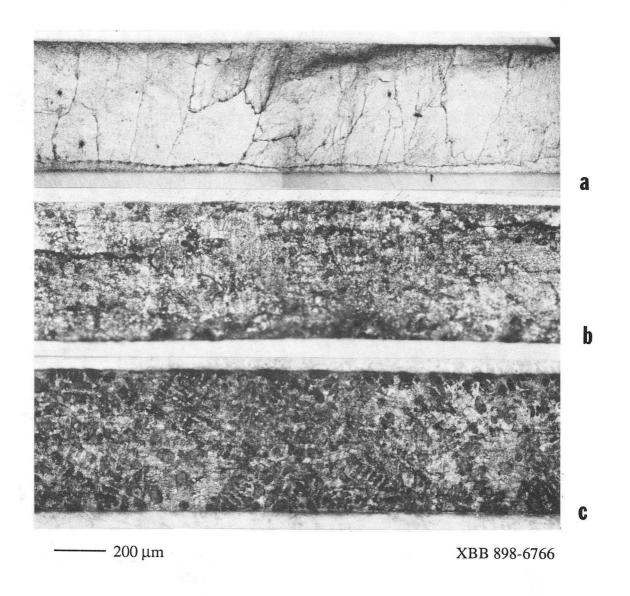


Fig. 21. Optical micrographs showing the surface relief following fatigue of (a) 63Sn-37Pb, (b) 50Sn-50Pb, and (c) 40Sn-60Pb joints.

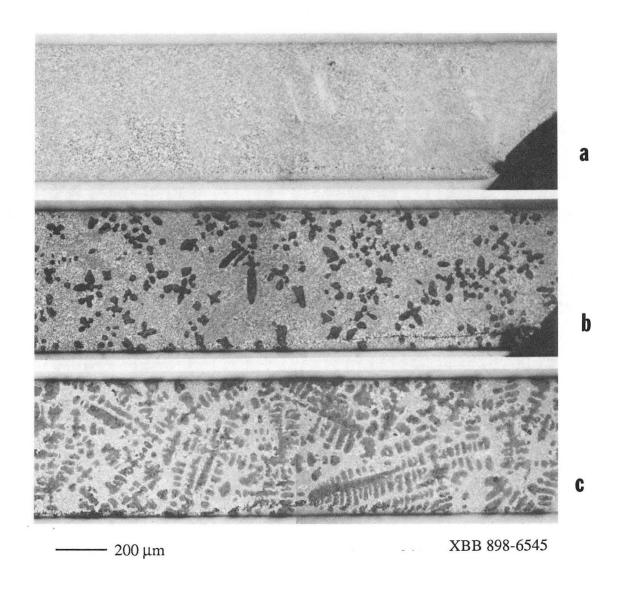
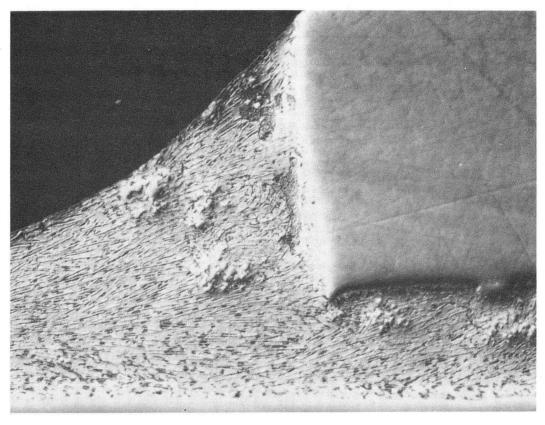


Fig. 22. Optical micrographs of the same samples in figure 21 after polishing, (a) 63Sn-37Pb, (b) 50Sn-50Pb, and (c) 40Sn-60Pb joints.



XBB 909-7875

<u>25μm</u>

Fig. 23. Optical micrograph of a eutectic Sn-Pb solder joint with Au protected layer on a conductor, showing dispersed Au-Sn intermetallics.

LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720