Mechanical Behavior of Plutonium and Its Alloys

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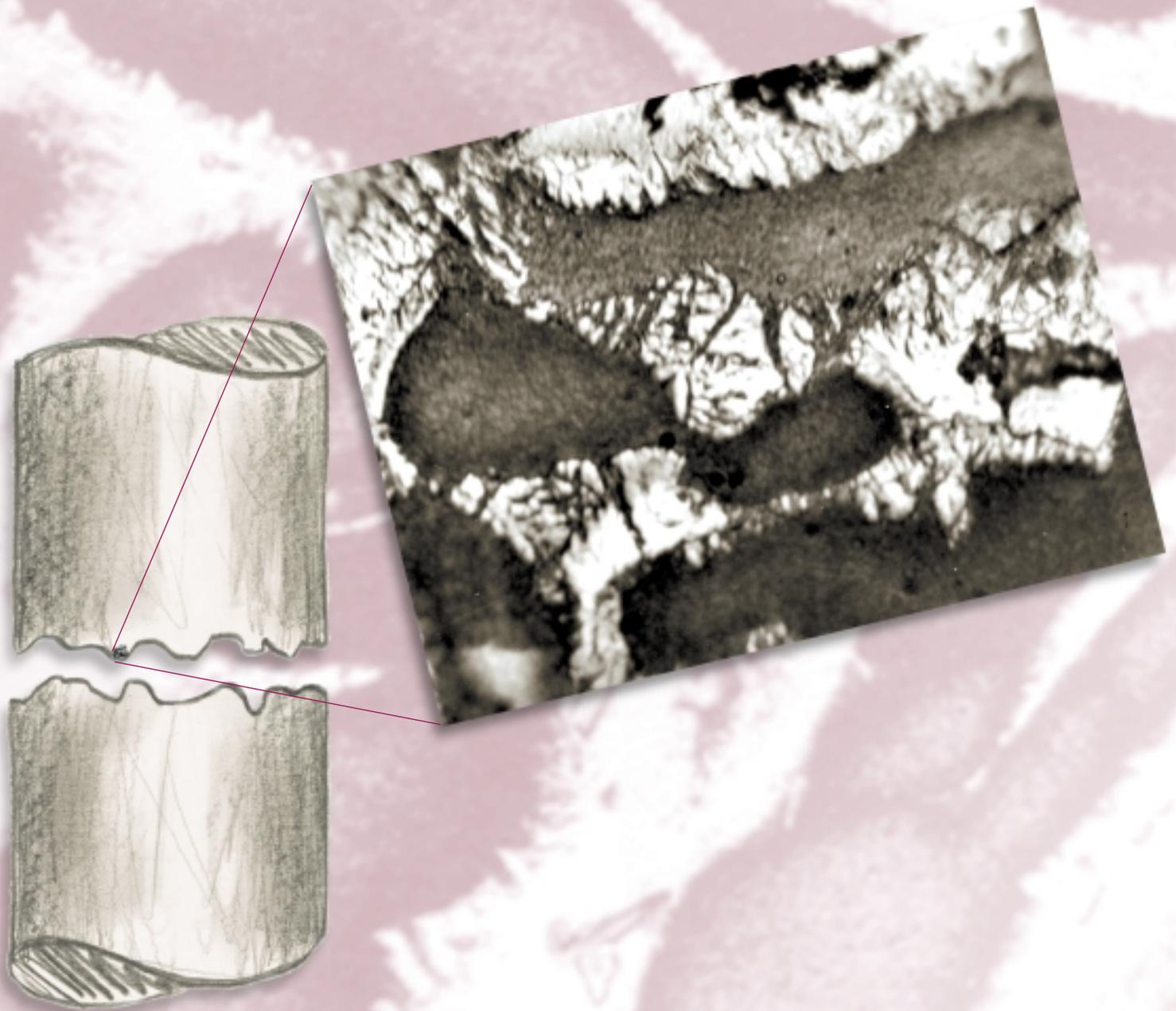
The current renaissance in plutonium research derives in large part from our need to predict the mechanical, or load-bearing, response of this material under different conditions. The Manhattan Project chemists and metallurgists learned enough in a very short time to make this fickle metal behave in an acceptable way during casting, pressing, machining, and assembly. Their achievement was all the more remarkable because only very small quantities of plutonium were available for study during most of the project (see the article "The Taming of '49'" on page 48). Stockpile certification in the absence of nuclear testing, as it is done today, requires that we have a much more thorough understanding of plutonium's structural and mechanical properties.

Plutonium exists in six different crystallographic phases before it melts at the relatively low temperature of 640°C. The two phases of greatest interest are the monoclinic α-phase, the stable form of unalloyed plutonium at room temperature, and the face-centered-cubic (fcc) δ-phase, which can be retained down to room temperature by the addition of a few atomic percent (at. %) of aluminum or gallium. The mechanical properties of these two forms of plutonium are as different as night and day. Although metallurgists have little experience with monoclinic structures (plutonium is the only metallic element that exists in this form), conventional wisdom and comparison with minerals that have monoclinic structures suggest that α-plutonium should be very brittle at room temperature. And indeed, this appears to be the case. Similarly, metallurgists' experience with fcc metals and alloys suggests that fcc δ-plutonium alloys should be very ductile and tolerant of flaws, and should have low strength. Again, such is the case for the δ-phase alloys.

Yet, plutonium and its alloys are full of surprises. In this article, we focus on some of their exotic mechanical behaviors in the hope that we can generate renewed scientific interest in this unusual metal. We also touch on the fundamental dichotomy in all structural materials—the inverse relationship between strength and ductility. How to make strong materials more ductile

(and tougher) and ductile materials stronger is a real challenge for all structural materials. For a thorough review of the conventional mechanical properties of plutonium, you can refer to the compendium of mechanical properties of engineering interest presented by Gardner (1980).

Renewed Interest in Fundamental Mechanical Properties

Mechanical properties are relevant to all aspects of manufacturing—from shaping to machining—as well as to the engineering and dynamic performance of nuclear weapons. Plutonium is the heart of the "nuclear trigger" of modern nuclear weapons. For decades, we could compensate for the gaps in our understanding of plutonium's complexities by testing nuclear devices underground at the Nevada Test Site. Today, we must be able to certify without nuclear testing that the nuclear weapons remaining in the United States stockpile are safe and reliable. We must also remanufacture plutonium components or extend their design lifetimes in the absence of testing.

Today's manufacturing engineer must know how all processing steps affect the evolution of microstructure in order to ensure that the final plutonium product may be substituted for original, certified, or "diamond-stamped," com-

ponents now in the stockpile. Variability in the manufacturing process and in the factors that cause such changes, such as impurity streams, must be reduced to previously unattained levels if we are to establish a quality-assured scheme for the manufacture of small numbers of units. In the past, plutonium components in weapons systems were specified simply on the basis of the chemical assay of the plutonium, the average component density, and adherence to required dimensions. Today, we must understand how microstructure affects mechanical properties in order to predict acceptable performance.

In the present nontesting environment, nuclear weapons physicists and engineers are using sophisticated computer models and calculations to assess performance. These computer models require realistic models of materials behavior, backed up by rigorous experimental data. Both engineering and dynamic performance, however, involve loading conditions that are not easily achieved in the laboratory. Hence, materials models must be guided not only by experiment but also by a fundamental understanding of the atomic processes governing the mechanical behavior of plutonium.

In light of those needs, we present some of the unusual mechanical properties that require study. Specifically, we will discuss anomalous plastic flow in α-plutonium and the role of stress-induced transformations in the fracture of
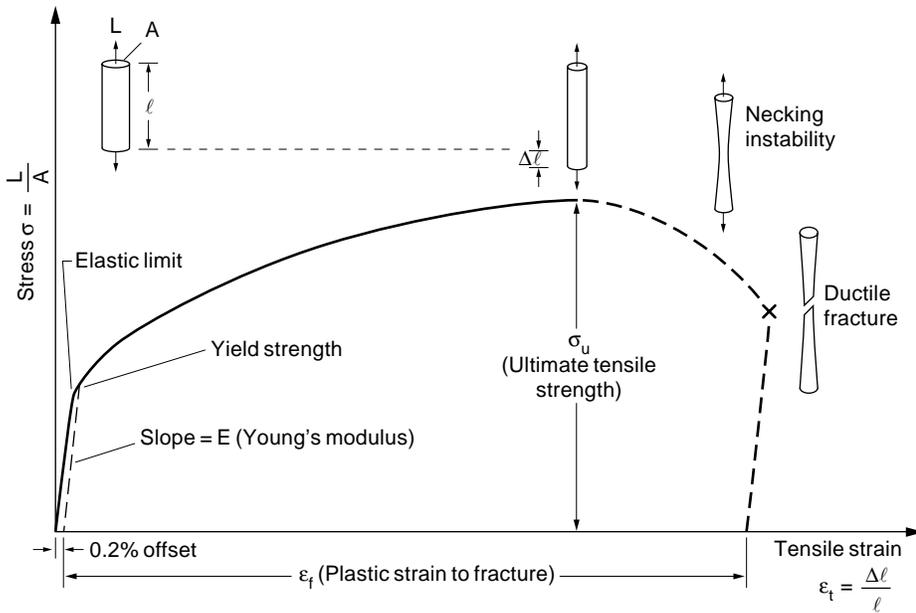
Figure 1. Tensile Stress-Strain Curve for a Typical Ductile Metal
The tensile test is the most common test used to measure mechanical properties. Round-bar or sheet samples are gripped at their ends and pulled at constant velocity (nominally, at constant strain rate) until they fail. Load and displacement of the sample are measured and plotted as stress σ (load/cross-sectional area) vs strain ε (sample elongation/original length). The elastic region, represented by Hooke's law ($\sigma = E\varepsilon$, where E is the elastic modulus known as Young's modulus), is linear and reversible. The point of deviation from linearity is called the elastic limit and marks the onset of permanent deformation, or plastic flow. Because the onset of deviation is often very gradual, the "yield strength" of a metal is defined as the stress at 0.2% permanent (or plastic) strain. Continued plastic flow beyond the elastic limit produces increasing stress levels—a process called work hardening. During this stage, the sample deforms uniformly, elongating and thinning while the volume remains constant, until work hardening can no longer keep up with the continuing increase in stress caused by the reduction in the sample's cross-sectional area. At this point, the stress goes through a maximum, called the ultimate tensile strength, and the sample begins to deform nonuniformly, or neck, before it fractures in a ductile manner. In soft, annealed fcc metals, the typical total plastic (or permanent) strain immediately prior to fracture is 20% to 50%.

α-plutonium and in the plastic flow of δ-phase plutonium alloys. However, we will first introduce both macroscopic engineering and microscopic concepts as a necessary background for the plutonium discussions.

Engineering Response

Structural materials are designed and fabricated based on their response to external loads, or stresses. The design engineer usually specifies high-strength materials that will strain, or deform, in an elastic manner under anticipated loads, meaning that the material will re- vert to its original dimensions when the load is released. When stressed beyond their elastic limit, many structural mate- rials fail abruptly, absorbing little energy. Among these materials are con- crete, many ceramics, and many thermosetting plastics. In contrast, most metals and thermoplastics (for example, polyethylene) are ductile, or malleable.

They deform extensively, beyond the elastic limit, as they absorb large amounts of energy. Consequently, these materials are much more tolerant of flaws, and they can be worked, or formed, into different shapes through a variety of processing techniques, such as injection molding, extrusion, rolling, and forging. The microstructural processes that allow these materials to deform plastically differ appreciably from one type of material to the next. In the thermoplastic polymer, especially during high-temperature processing, molecules flow over or move past each other much as they do in a liquid. In metals, as we will see, plastic deforma- tion occurs by the motion of line defects known as dislocations.[1]

A material's mechanical strength, or the stress it can withstand before it deforms or fractures, is typically mea- sured by a standard uniaxial tensile test. Round or sheet samples are pulled along one axis at constant velocity while the deformation, or strain, incurred is measured. Ductile materials show limited elastic response (low yield strength) followed by extensive plastic deformation and ductile fracture, as shown schematically in Figure 1. In Figure 2(a) we show that the pluto- nium-gallium (Pu-Ga) δ-phase alloys follow this pattern, whereas unalloyed α-plutonium is strong and brittle like cast iron: It has an elastic response with very little plastic flow until the stresses become so high that the metal fails by brittle fracture. We note for later refer- ence that the strength of the unalloyed α-phase decreases dramatically with increasing temperature—see Figure 2(b)— much like the strengths of many body-centered-cubic (bcc) and hexagonal-close-packed (hcp) metals. In contrast, the yield strength of the

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[1]Many times, ductility and malleability are confused with toughness. Strictly speaking, tough- ness, or fracture toughness, refers to the metal's ability to resist crack or flaw growth. Stresses are extremely high in the region just ahead of the tip of a crack, and it is thus the stress-dissipating capacity of the microstructure, or the material's toughness, that becomes important when catastrophic crack growth is a concern.
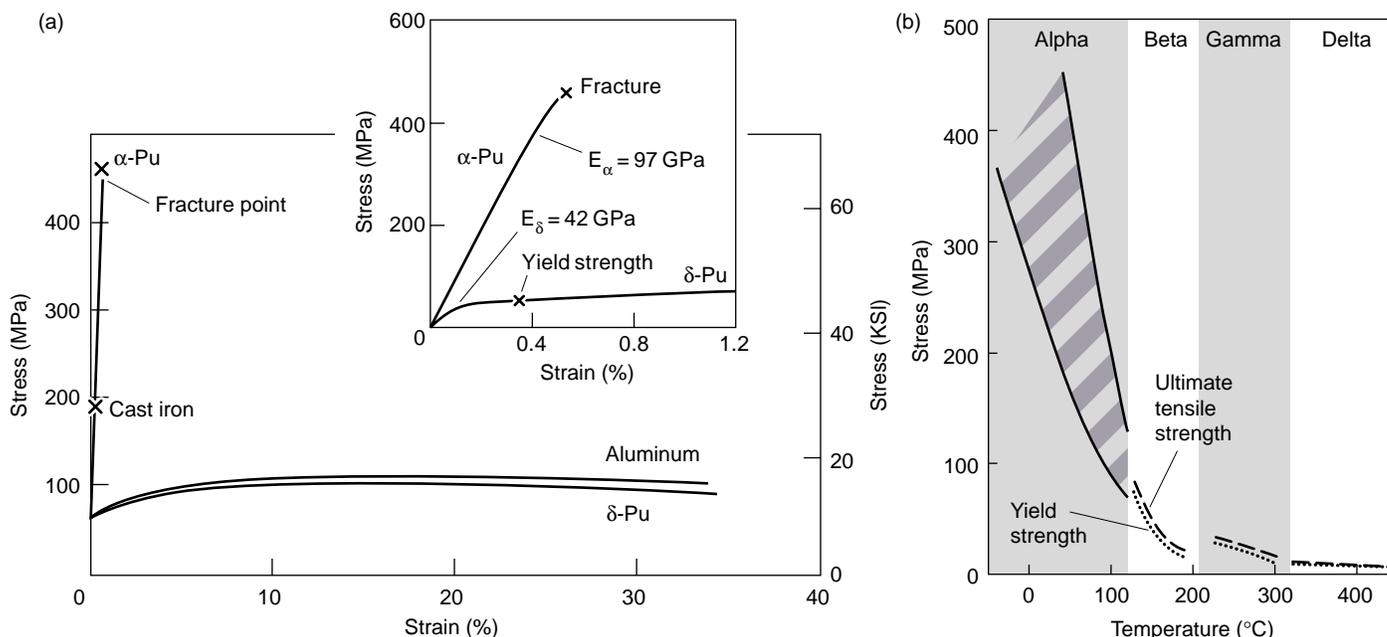
Figure 2. Tensile Stress-Strain Response for Plutonium at Ambient and Higher Temperatures
(a) Typical uniaxial stress-strain responses at room temperature for unalloyed monoclinic α-plutonium and fcc δ-phase Pu–1.7 at. % Ga alloy are compared with the response for aluminum. For α-plutonium, the elastic limit essentially coincides with the fracture strength. Very much like aluminum, the ductile Pu–1.7 at. % Ga alloy work-hardens before failing by ductile fracture. (b) The typical tensile-test results for unalloyed polycrystalline plutonium shown here are based on those reported by Gardner (1980). They indicate overall trends in the dependence of strength on temperature for the different plutonium phases. The strengths of the α- and β-phase are very sensitive to temperature, those of the γ-phase less so, and the δ-phase has little strength over its entire range of stability. The strength of the ε-phase is very low and time dependent because its more-open bcc structure exhibits very high diffusion rates. These data represent the work of several investigators, different purity materials, and different testing speeds. Except for α-plutonium, the upper curves designate the ultimate tensile strength and the lower the yield strength. For α-plutonium, the yield and ultimate strengths show tremendous scatter and are not easily discernable. Hence, we simply show a band of strength values. (Reproduced with permission from H. R. Gardner and the American Nuclear Society, *Plutonium Handbook*, page 68, 1980.)

unalloyed δ-phase behaves like most other fcc metals, showing little temperature dependence.

The electronic structure and the resulting cohesive forces holding the metal together are directly responsible for the metal's elastic response. Generally, metallic bonding produces high cohesive forces and high elastic constants (stiffness). Metallic bonding is not very directional because the bonding (or valence) electrons are shared throughout the crystal lattice (see the article "Plutonium and its Alloys" on page 290). Consequently, metal atoms tend to surround themselves with as many neighbors as possible, forming close-packed, relatively simple crystal structures. In plutonium, however,

the narrow conduction bands and high density-of-states of the 5f electrons make it energetically favorable for the ground-state crystal structure to distort to a low-symmetry monoclinic lattice at room temperature. Plutonium adopts the more typical symmetric structures only if the temperature is raised or if the metal is suitably alloyed.

The variation of elastic moduli with direction in a crystal lattice provides important information about the cohesive electrostatic forces—the balance between attractive forces that act at long range vs the repulsive forces that dominate at short range. The directionality of the elastic moduli is partially averaged out in polycrystalline samples if the polycrystalline aggregates are sufficiently

random. For that reason, measurements of elastic moduli must be done on high-quality single crystals. Unfortunately, the multiple phase transformations in plutonium make crystal growth immensely difficult, and only very few studies have been conducted on single crystals of either α-plutonium or δ-phase plutonium alloys (see the article "Preparing Single Crystals of Gallium-Stabilized Plutonium" on page 226).

Although a few single crystals of α-plutonium were grown in the 1960s (Liptai and Friddle 1970), elastic constants have not been studied systematically. Limited elastic-modulus measurements performed as part of Liptai and Friddle's deformation studies, which will be reported next,
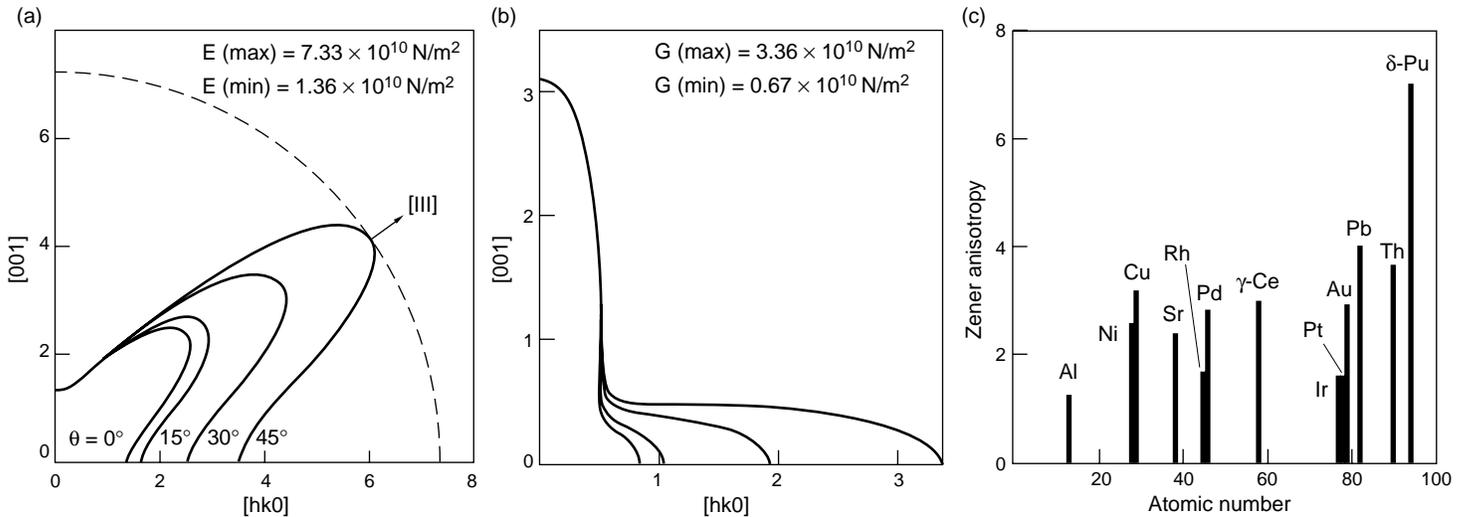
Figure 3. Single-Crystal Results for Elastic Moduli of δ-Plutonium

The ultrasonic velocity measurements reported by Moment and Ledbetter (1976) on δ-phase Pu–3.4 at. % Ga single crystals show surprising anisotropy—the crystals are very stiff in tension and compression and soft in shear in the [111] direction and vice versa in the [100] direction. In this case, the Zener anisotropy, $A = 2C_{44}/(C_{11} - C_{12})$, is very large when compared with that of other fcc metals, but it is about equal to that of the alkali metals (sodium, potassium, and lithium). A polar plot of Young's modulus with crystal direction is shown in (a). Each curve lies in a plane containing [001] at an angle θ from [100]. The polar plot shown in (b) is of the shear modulus with crystal direction. Plot (c) shows the Zener anisotropy for fcc metals.

showed variations of greater than a factor of 2 in the elastic modulus with crystal orientation. Young's modulus (the average elastic constant for uniaxial tension) for polycrystalline α-plutonium is almost twice that of the δ-phase alloy (see Figure 2). However, even polycrystalline α-plutonium is not considered very stiff; its Young's modulus is approximately equal to that of titanium, but only half of that of steels. Even by comparison with other fcc metals, δ-phase plutonium alloys are very soft. For example, Young's modulus of δ-phase plutonium alloys is 40 percent lower than that of pure aluminum. Elastic-constant measurements on textured polycrystalline materials could also provide us with some indication of the directionality of single-crystal properties. Unfortunately, no such studies have been reported for textured polycrystalline α-plutonium.

The elastic constants of single-crystal δ-phase plutonium alloys show surprising anisotropy. Only one set of such measurements has been made at room temperature (Moment and Ledbetter 1976) on a small single crystal of Pu–3.4 at. % Ga alloy. As shown in Figure 3, the elastic moduli in the "soft" and "stiff" directions differ by more than a factor of 5—the largest variation for any fcc metal. Fortunately, much of this anisotropy of elastic moduli is averaged out in δ-phase plutonium polycrystals.

Unlike elastic constants, which vary directly with the strength of the cohesive forces between the atoms, the mechanical strength and plastic properties of metals depend on cohesive forces in a subtle manner. Metals yield, or flow plastically, at stress levels as low as 0.01 percent of the theoretical stresses required to pull the atoms apart or cause entire rows of atoms to slip over each other. This enormous reduction in strength compared to the theoretically predicted value results from the influence of defects, principally dislocations. On the other hand, the interactions of dislocations with each other and with other

microstructural defects increase the strength of ductile metals considerably by a process called work hardening. In brittle materials, plastic flow (that is, the ability of dislocations to move) is severely limited. Therefore, the strength of those materials is reduced dramatically by the presence of microscopic cracks or other flaws. Before discussing some of the anomalous plastic-flow properties of plutonium, we provide a brief description of dislocations and twinning as background for understanding plastic flow and work hardening in plutonium.

Dislocations and Twinning

More than 20 years before dislocations were actually observed in a transmission electron microscope, their existence was postulated to explain why the observed yield strengths of metals are so much lower than their theoretical values. A dislocation is a line defect formed by the presence of an extra half

Figure 4. Dislocations and Their Role in Facilitating Slip

A dislocation is a crystalline line defect that enables one crystal plane to slide over another at much-smaller applied shear stresses than would be required in a perfect crystal. There are two basic orientations, edge and screw. Most dislocations are actually curved or wavy, with mixed character (varying from pure edge to pure screw orientation).

(a) An edge dislocation can be simply imagined as an extra half plane of atoms (shaded red) inserted into a crystal. The dislocation line created by the edge of this extra half plane is symbolized with a perpendicular sign, ⊥, shown in red. When the sign points up, the extra half-plane is up and vice versa. The distortion in the periodic lattice caused by the dislocation is represented by the Burgers vector b, which is defined by lack of closure of the Burgers circuit drawn around the dislocation. The dislocation is completely described by its Burgers vector b and the orientation of the dislocation line. Because the Burgers vector is perpendicular to the dislocation line, a given edge dislocation can move only on one slip plane. The dislocation line also marks the boundary between the deformed region of the slip plane (shaded in blue) and the undeformed region.

(a) Extra half-plane / τ / b / Direction of dislocation glide / Core of dislocation / Dislocation line
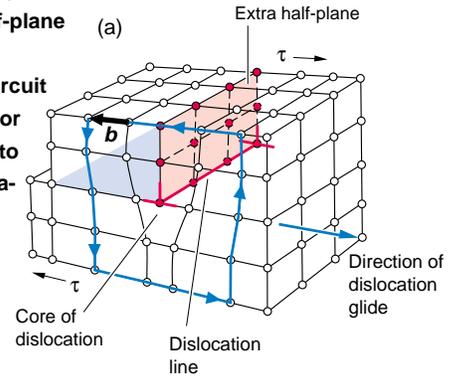
(b) This series of cross-sectional views of the edge dislocation shows how it moves one atomic distance at a time through an entire crystal and thereby produces a step of one Burgers vector on the crystal surface. As illustrated at the bottom of each view, the edge dislocation acts like a wrinkle in a rug, reducing the interatomic forces in its vicinity and allowing an entire plane of atoms to slip over another at a reduced stress. Continued application of shear stress (τ) will move these dislocations by repeated steps along the slip planes of the crystal, a process called dislocation glide. The dislocation slip planes and slip directions are the same as those for shear of entire atomic planes in perfect crystals.

(b)

(c) Dislocation line / Extra half-plane / Direction of dislocation glide / Dislocation core / b / τ / τ
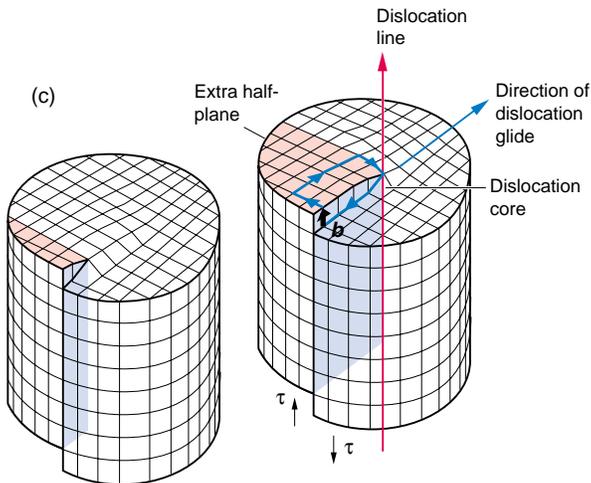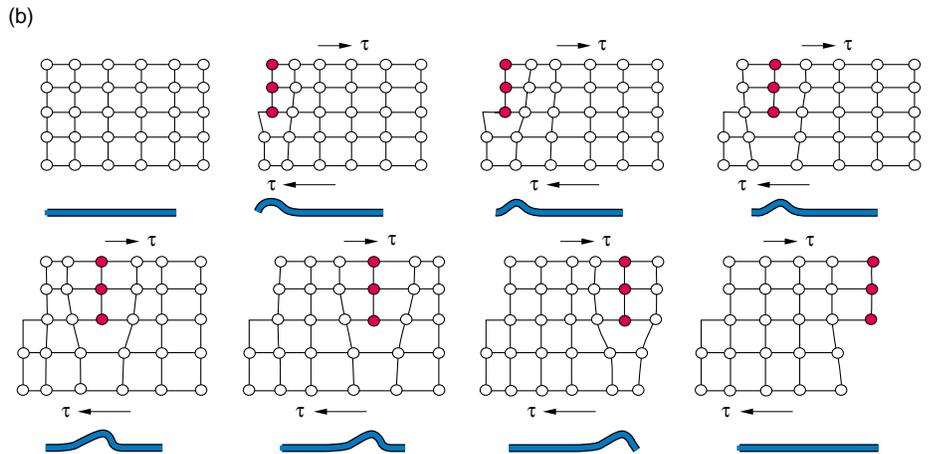
(c) A screw dislocation can be imagined as a tear that propagates through the crystal, creating an extra half plane (shaded in red) perpendicular to the dislocation line (red). The resulting distortion resembles the levels of a spiral staircase, or the thread on a screw. The screw dislocation itself is the pole about which the spiral ramp circles. In a screw dislocation, the Burgers vector b is parallel to the dislocation line. Hence, any plane that contains a screw dislocation can act as its slip plane. Again, the dislocation line marks the boundary between the deformed region of the slip plane (shaded in blue) and the undeformed region. The Burgers circuit for a screw dislocation also defines the Burgers vector as the lack of closure around the dislocation.

(d) A mixed dislocation is a combination of a screw and an edge orientation. Note that the dislocation line for a mixed dislocation is curved.

(d) Dislocation line / b / Screw dislocation / b / Edge dislocation
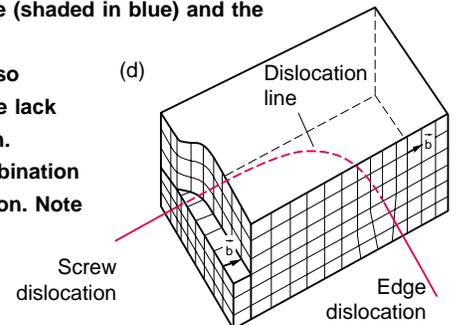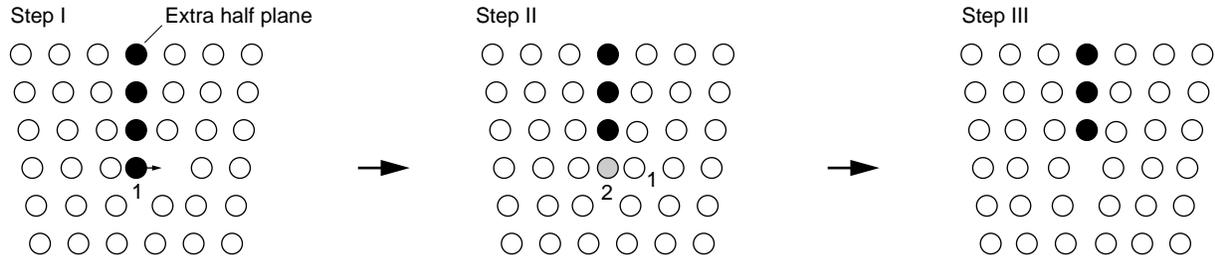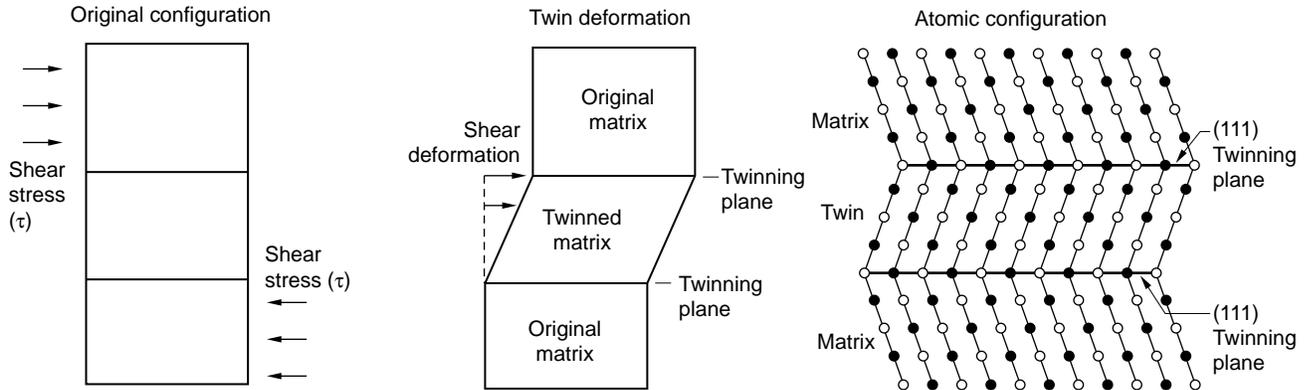
Figure 5. Climb and Twinning

(a) The positive climb of an edge dislocation is illustrated here. The extra half plane is perpendicular to the plane of the diagram and is indicated by filled circles. For the dislocation to climb, a vacancy has moved up (Step I) to a position just to the right of atom 1, one of the atoms forming the edge of the extra plane. If atom 1 jumps into the vacancy (Step II), the edge of the dislocation loses one atom, and atom 2 (shaded circle) becomes the next atom of the edge (lying just below the plane of the paper). If all other atoms that formed the original edge of the extra planes move off through interaction with vacancies, the edge dislocation will climb one atomic distance in a direction perpendicular to the slip plane (Step III). (b) At left, the shear stress applied to the original configuration produces a twin deformation. The atomic arrangement at the twinning planes in an fcc crystal is shown at right. The solid and open circles represent atoms above and below the plane of the paper, respectively. The interface between the original matrix and its mirror image is exactly parallel to the twinning plane. In this case, the twin and parent lattices match perfectly at the interface (called a coherent twin boundary).

plane of atoms in a crystal. The two basic types of dislocations, edge and screw, are defined in Figure 4. The figure also shows schematically how dislocations move, or glide, along slip planes in response to applied shear stresses(τ). Each step of the motion requires only a slight rearrangement of the atoms in the vicinity of the extra half plane, thereby reducing the enormous shear stresses that would otherwise be required to move one entire plane of atoms over another. The movement of a dislocation through a crystal produces conservative displacement of the crystal in much the same way that a rug can be incrementally

moved across a floor when one pushes a wrinkle, or "ruck," in the rug across its length. Moreover, as it moves along the slip plane, the dislocation defines a moving boundary between plastically deformed and undeformed material on that slip plane.

Dislocation Glide. Slip, also called dislocation glide, can occur in metals because the metallic bond is not very directional, and atoms can slide past one another relatively easily for long distances without breaking bonds. In high-symmetry metallic crystals, dislocations can adopt a configuration in which cohesive forces offer very little

resistance to their glide motion along the close-packed planes, allowing most metals to undergo large plastic deformations before fracture. However, many hundreds of thousands of dislocations must move across a slip plane to produce a visible slip line on the surface. Passage of a dislocation leaves the crystal in the same atomic configuration in which it was before. Hence, the lattice is unchanged, and volume is conserved. In other words, plastic deformation—whether caused in tension, compression, in a rolling mill to make thin sheet, or in a forging to make a complex shape—produces the desired change of shape without a change in volume.

Dislocations tend to form at sites of imperfection either during solidification and subsequent cooling or during plastic deformation. The density of dislocations equals the number of dislocations passing through a unit area. Unlike lattice vacancies, dislocations do not lower the Gibbs free energy of a crystal, but they are unavoidable because tiny stresses cause them to form. Even with the greatest care, it is virtually impossible to solidify or anneal a typical material with a dislocation density below 10^4 dislocations per centimeter squared (dislocations/cm^2).

Dislocations are also a natural consequence of metallic-crystal growth from the liquid, or supersaturated vapor, because the transfer of atoms to the growing crystal occurs more readily along a step or ledge, than on a perfect surface. Typical annealed metals and alloys contain 10^7 dislocations/cm^2. Heavily deformed (cold-worked) metals and alloys contain on the order of 10^{11} dislocations/cm^2 because dislocations are created during cold working. Paradoxically, metals can be made to approach their theoretical strength by either of two opposite methods: removing virtually all dislocations, as in the growth of very fine metal whiskers, or generating excessively large numbers of dislocations that will impede each other's motion to increase strength.

Dislocation Climb. During dislocation glide at low temperatures, edge dislocations are confined to their slip plane, whereas screw dislocations may "cross-slip" from one slip plane to another. At temperatures on the order of half the melting temperature of a material, edge dislocations begin to move by a mechanism known as dislocation climb. In this process, the inherent stress field surrounding the edge dislocation line induces vacancies to migrate sequentially to positions along that line. Each time a vacancy attaches to the edge dislocation, that small segment has climbed one atom spacing out of its previous glide plane—see Figure 5(a). As the process continues through many

repetitions, the affected dislocations move appreciable distances and cause the bulk material to exhibit macroscopic "creep," that is, elongation and thinning on a macroscopic scale. Climb is fundamentally different from glide in several ways: Climb is sensitive to normal stress (tensile or compressive for positive and negative climb, respectively), whereas glide results from a shear stress. Also, climb requires enough energy to create or annihilate vacancies (for negative and positive climb, respectively). Climb thus requires temperatures at which vacancies migrate easily—typically above half of the absolute melting point.

Twinning. Metals sometimes respond to shear by a process called mechanical (or deformation) twinning. In this organized transformation, shear stresses cause a portion of a crystal to become the mirror image of its original crystal structure. The plane of symmetry between the two portions of a twinned crystal is called the twinning plane—see Figure 5(b). In the simple lattice shown, a homogeneous shear has caused each atom in the twinned region to move a distance proportional to its distance from the twinning plane. The atoms move less than one atomic spacing and produce an orientation difference across the twinning plane. In contrast, dislocation glide produces no orientation difference across a slip plane, and it occurs in discrete multiples of atomic spacing. Twinning can, however, be considered a variant of dislocation glide, involving the motion of partial, rather than complete, dislocations. Nucleation, not propagation, appears to be the typical rate-limiting step for twinning.

The lattice strains required for twinning are very small, making the total deformation achieved quite small. However, if the orientation of the crystal is changed, twinning may enable new slip systems to activate new slip modes. This process is therefore especially important in metals with a limited number of slip systems, such as the hcp metals.

Deformation twinning is not prevalent in fcc crystals, occurring only in some fcc metals and alloys at very low temperature. It does, however, occur more readily in bcc and hcp metals, especially at low temperatures or under shock-loading conditions. Twins can also form during annealing, especially in fcc metals after they have been deformed.

We have provided only a brief introduction to dislocation basics. For a comprehensive treatment of dislocations in materials, refer to Hirth and Lothe (1982). We now return to the discussion of plutonium's mechanical behavior.

Anomalous Plastic Flow in α-Plutonium

Manifestations of Low Crystal Symmetry in Single-Crystal Experiments. Figure 6(a-c) shows the monoclinic structure of α-plutonium in three views that emphasize its similarity to a distorted hexagonal lattice. Metallurgists have very little experience with monoclinic structures—these are typically in the domain of geologists. In geologic minerals, one finds that plastic deformation by dislocation glide occurs on a single plane of the {001} family. Similarly, metal crystals of lower symmetry slip relatively easily on a single slip plane. For example, hcp metals that are perfectly packed (that is, the ratio of lattice constants $c/a = 1.633$) slip on the basal, or close-packed plane in the three close-packed directions (refer to the box "Atomic Packing and Slip Systems in Metals" on page 308 in the article "Plutonium and Its Alloys"). Crystals of hcp magnesium, zinc, and cadmium with $c/a > 1.633$ are also observed to slip easily on the basal planes. On the other hand, hcp titanium, zirconium, and hafnium with $c/a < 1.633$ slip more easily on the family of prism planes.

Carefully controlled experiments on single crystals deformed at different orientations are required to sort out the

(a)

(b)

(c)
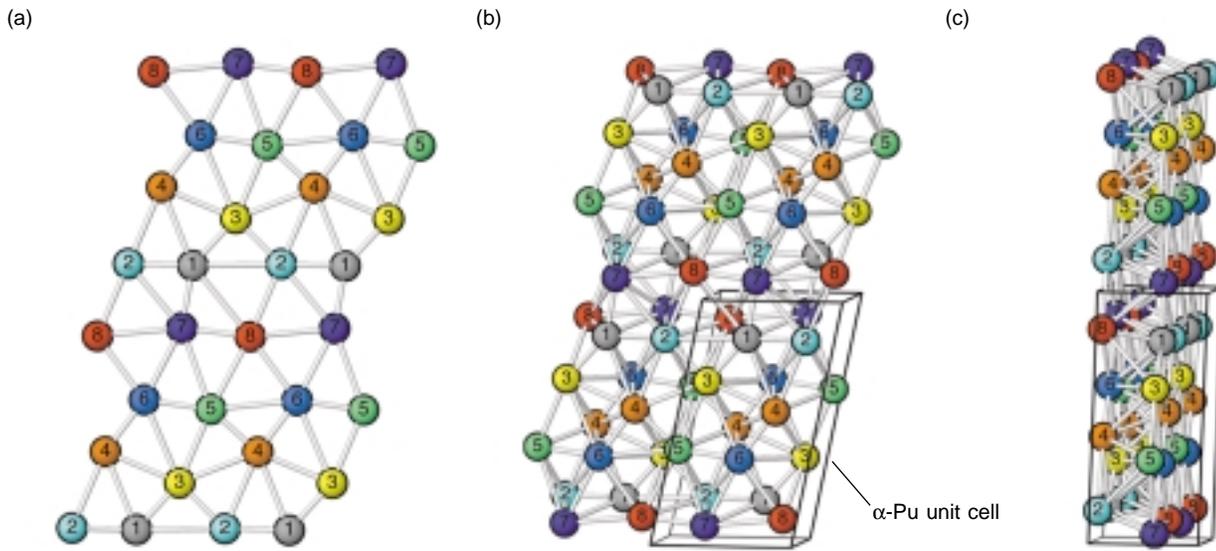
α-Pu unit cell

Figure 6. Slip Systems in α-Plutonium Single Crystals
(a) The (020) plane of the α-plutonium monoclinic crystal resembles an hcp plane. (b) Two stacked (020) planes of the crystal contain
four unit cells. Although the bonds fall into two groups (long bonds between ~3.19 and 3.71 and short bonds between ~2.57 and
2.78), each of the eight numbered sites is crystallographically unique. Lawson et al. (1996) refer to α-plutonium, which has 16 atoms
per unit cell with eight distinct lattice positions, as a self-intermetallic material. (c) Here is a 90° rotation of (b), showing that (020)
plane layers in α-plutonium lie in almost flat close-packed planes, as in an hcp structure. For more details on the structure, see
Figure 25 on page 331 of the article "Plutonium and Its Alloys." (Reproduced with permission from the Metallurgical Society.)

(d)

1 mm

A

B

A   B

~0.5 mm

(e)

$(\bar{1}00)$

$(\bar{4}1\bar{1})$

$(\bar{2}1\bar{3})$

$(\bar{4}15)$

$(\bar{1}02)$

$(\bar{3}2\bar{3})$

$(00\bar{1})$

(010)

(001)

$(11\bar{4})$

(112)

(111)

(118)

(213)

(101)

(100)
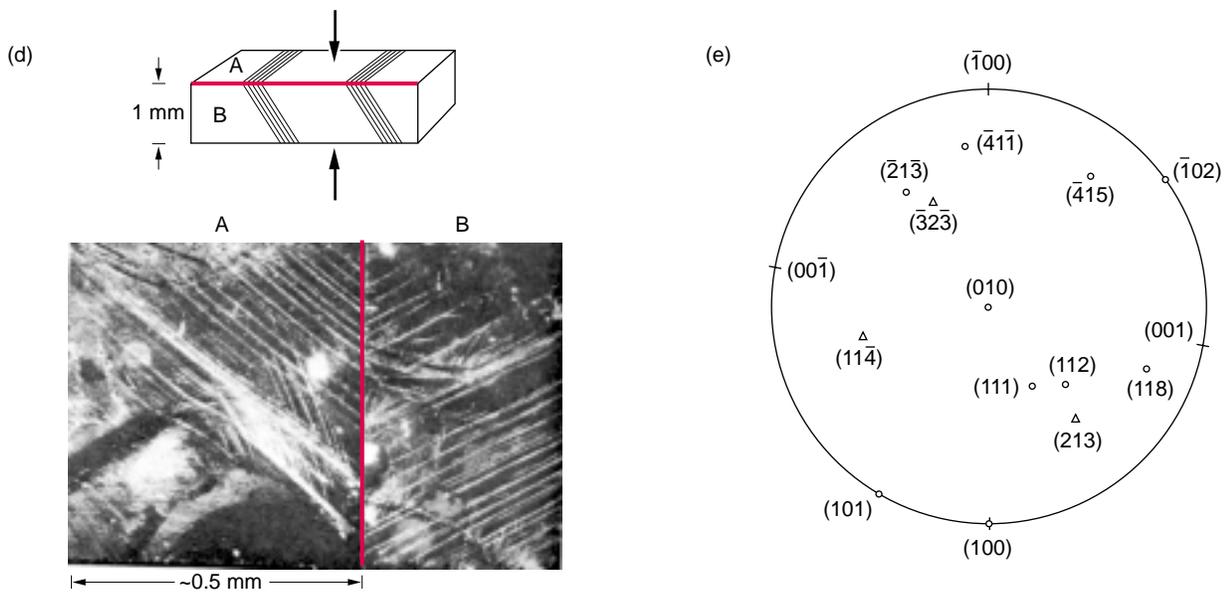
(d) A room-temperature deformation is illustrated, which resulted from compression of a high-purity single-crystal bar of α-plutonium
grown under pressure at Argonne National Laboratory (Argonne). Slip traces are seen on polished surfaces. The micrographs are
placed to match traces from surface A and B (see the boundary between these surfaces). (e) Shown here is a stereographic projec-
tion of poles of planes along which slip was observed during experiments on single-crystal and polycrystal α-plutonium at Argonne
(Liptai and Friddle 1970) and Los Alamos (Bronisz and Tate 1965). For this projection, a cube face is parallel to the projection plane,
the x- and y-axis lie in the projection plane so that the poles of planes (100) and (001) are on the basic circle, and the z-axis is
normal to the projection plane so that the pole of plane (010) is at the circle's center.

fundamental behavior of dislocations in a material. But the difficulty of growing single crystals of α- or δ-plutonium has precluded all but the few experiments conducted on α-plutonium single crystals and polycrystals by Bronisz and Tate (1967) and Liptai and Friddle (1970). The results of those experiments, shown in Figure 6(e), were very unexpected. Because the α-plutonium structure is like a distorted hexagonal lattice, α-plutonium was expected to behave like hcp metals and low-symmetry ceramics and minerals. Specifically, it was expected to slip on a single family of slip planes, namely, the (020) planes, which are the closest-packed and the only atomically flat planes in the monoclinic α-structure—see Figure 6(a–c).

Quite surprisingly, a single crystal of α-plutonium placed at different orientations and deformed in compression at room temperature (single-crystal samples were too small to test in tension) exhibited slip on many different slip planes although, predominantly, on one plane for a given orientation. Some evidence of wavy slip traces was also found, suggesting that slip occurred on several planes in a single direction (as it does often in bcc metals).

In many metals, twinning becomes a predominant deformation mode when slip is difficult. Consequently, our assumption that slip was difficult on planes other than the (020) planes led us to expect twinning to be a predominant deformation mode in α-plutonium. Instead, twinning occurred only sporadically at room temperature, and was judged not to be an important deformation mechanism. Most α-plutonium single crystals were also found to be quite brittle (< 1 percent plastic strain) in compression, whereas a few samples stretched a respectable 13 to 16 percent. For comparison at both extremes, a properly oriented hcp magnesium single crystal can stretch out to a ribbon of four or five times its original length at room temperature and at shear stresses as low as 0.7 megapascal, whereas single crystals of hcp beryllium or

titanium exhibit only limited slip at very high resolved shear stresses (35 to 110 megapascals).

Clearly, we need more experiments on single crystals to understand slip and the fundamental behavior of dislocations in monoclinic α-plutonium. Likewise, modeling with realistic interatomic potentials would help guide critical experiments. We would like to understand, for example, if the "self-intermetallic" nature of α-plutonium described by Lawson et al. (1996), that is, the fact that the unit cell has eight distinctly different atoms of different sizes—refer to Figure 6(a–c)—influences the operation of different slip planes, as documented in Figure 6(e).

Effects of Low Crystal Symmetry in Polycrystalline Samples. The number of active slip systems and the relative lattice resistance of different slip systems are very important in determining the mechanical response of polycrystalline metals. An individual grain in a stressed polycrystal feels a strong restraining effect from the surrounding grains of different orientations because the net cohesive forces holding the grains together tend to prevent the opening up of voids or cracks. Consequently, stress concentrations build up near grain boundaries and grain triple points. Only very complex modes of deformation involving multiple slip systems within the grains can relieve those stresses. G. I. Taylor (1934) showed that no less than five independent slip systems (or other modes of shear deformation) must operate to maintain continuity in polycrystalline materials. Since the very high symmetry of fcc crystals leads to 12 equivalent slip systems (four equivalent close-packed planes and three close-packed directions in each plane), fcc materials such as δ-phase plutonium alloys easily meet those constraints and therefore exhibit extensive ductility.

Polycrystalline materials of lower symmetry do not have the requisite number of equivalent slip systems for easy dislocation glide. Instead, other

slip systems (with higher lattice resistance) or other deformation modes, such as twinning, become operative, raising the stress required for deformation and making these materials more prone to fracture. Despite having many different planes, α-plutonium is unlikely to have five slip systems operate at once at room temperature. Furthermore, the extent of slip in α-plutonium single crystals is typically very limited. Consequently, we understand why polycrystalline α-plutonium is macroscopically brittle at room temperature in tension, typically exhibiting less than 0.1 percent plastic strain to failure, as shown in Figure 1.

Although α-plutonium is relatively strong at room temperature (typical tensile strength of 350 to 500 megapascals), its limited number of slip systems means it has little resistance to brittle crack propagation under tensile loads. The lack of plastic accommodation by slip also makes α-plutonium particularly prone to forming microcracks (which are virtually impossible to avoid during solidification because of large volume changes caused by phase transformations during cooling). Strength measurements in α-plutonium show scatter of ± 30 percent—see Figure 2(b)—because of the variation in number and propagation of microcracks. In addition, large grains lead to greater stress concentrations and more microcracks, which reduce the strength, as does the presence of second-phase inclusions.

Finally, polycrystalline materials with a limited number of slip systems tend to develop strong preferred orientation (or texture) when they are plastically deformed. In contrast to the anisotropy of elastic constants, which has little effect on macroscopic mechanical properties, texture, or plastic anisotropy, can have large mechanical effects because the different slip planes in aligned grains will present strongly varying lattice resistance to dislocation glide. Plastic anisotropy is prevalent in hcp polycrystals, for example, and strong textures can be developed in

deformed polycrystalline α-plutonium as long as it is deformed with sufficient confinement (as during compression or extrusion) to avoid microcracking and fracture. Very strong textures have also been created in polycrystalline α-plutonium by the application of stress during the β to α transformation, as reviewed by Nelson (1980).

Although no detailed experiments on texture formation in polycrystalline δ-phase alloys have been conducted, preliminary information suggests that these fcc alloys behave much like most other fcc alloys and do not develop strong textures. The very large elastic anisotropy in these alloys (see Figure 3) does not play a strong role in plastic deformation—most likely because the lattice resistance for dislocation glide is very low and there are 12 equivalent slip systems in fcc crystals.

Before discussing anomalous time-dependent plastic flow in plutonium, we introduce the deformation mechanisms that are expected at different temperatures. Our discussion focuses on how the collective motion of dislocations determines those deformation mechanisms.

Basic Kinetics of Plastic Flow in Polycrystalline Materials

The strength of a solid, or the stress at which it yields and begins to flow plastically, is not fixed. Instead, it depends on strain, strain rate, and temperature. On the atomic scale, plastic flow is a kinetic process in which crystal defects, such as lattice vacancies and dislocations, move in response to shear forces. In turn, those movements produce macroscopic changes in shape. Dislocation glide and climb were already discussed. Other atomic-scale processes by which defects move through the material and cause deformation include the diffusive flow of individual atoms, diffusion and defect motion in grain boundaries producing grain-boundary sliding, mechanical twinning, and others. Which

process is dominant changes, depending on the homologous temperature, T/T_m.

In their theoretical treatment of plastic flow, Frost and Ashby (1982) refer to defects as the "carriers" of deformation, much as an electron or an ion is the carrier of charge. And just as an electric current is proportional to the density and velocity of the electrons, the deformation rate, or shear strain rate, $\dot{\gamma}$, is proportional to the density of deformation carriers (mainly dislocations) and the velocity at which those defects move through the crystalline grains.

Each atomic-scale mechanism for the motion of defects leads to a different model equation for the strain rate as a function of stress, temperature, and material structure at that time (including dislocation densities and other microstructural properties, as well as material properties). The parameters in these rate equations are determined from experiments such as tensile tests at constant strain rate, an example of which is illustrated in Figure 1. Another common test is the creep test, in which materials are subject to constant load while the sample's change in length is measured as a function of time.

Based on these model-derived equations and measured strain rates, Frost and Ashby developed deformation-mechanism maps for metals, ceramics, and some minerals that show the regions of stress and temperature over which each deformation mechanism is dominant. (A map of pure aluminum is shown in Figure 7, and the dominant mechanisms at low and high homologous temperatures are illustrated in Figures 8 and 9, respectively.) The maps illustrate steady-state deformation behavior over a large range of stress levels and temperatures. They show calculated contours of constant strain rate produced by the appropriate superposition of all the deformation mechanisms at work at a given temperature and stress.

We do not have sufficient experimental information or theoretical understanding to construct such maps

for plutonium and its alloys. Instead, we present a brief review of the deformation mechanisms that lead to both the steady-state behavior represented on those maps and the transient behavior measured, for example, in a tensile test.

At the upper end of the applied shear-stress region in Figure 7 is the ideal, or theoretical, shear strength. Above that stress level, a perfect crystal, or one in which all the defects were pinned, would cease to be elastic and would fail catastrophically. Ideal strengths are calculated from a suitable interatomic potential. Some of the estimates using a Lennard-Jones potential place the ideal strengths of metals (at 0 kelvins) at values of 0.05 to 0.1 of the shear modulus (μ)—very high stress levels that are essentially never reached in practice.

Below that stress level and at low homologous temperatures (typically $T/T_m < 1/3$), the dominant deformation mechanism is dislocation glide. On the atomic scale, the motion of dislocations is limited by the inherent periodic resistance posed by the atomic structure of the lattice (known as the Peierls stress) and by discrete obstacles such as other dislocations, solutes or precipitates, and grain boundaries (see Figure 8). We have already discussed the limited capacity of polycrystalline α-plutonium for dislocation glide. On the other hand, in fcc aluminum and δ-phase plutonium alloys, dislocation glide is easy because 12 equivalent slip systems are operative, all with extremely low lattice resistance at all temperatures. Those systems therefore exhibit low strength and high ductility. Also, on the steady-state map for aluminum (Figure 7), the stress required for steady-state deformation through dislocation glide shows very little temperature or strain-rate dependence, again because the slip systems are numerous and have low lattice resistance.

However, during transient deformation, such as in a tensile test at room temperature, the atomic-scale behavior of these metals changes dramatically. Instead of exhibiting steady-state glide,
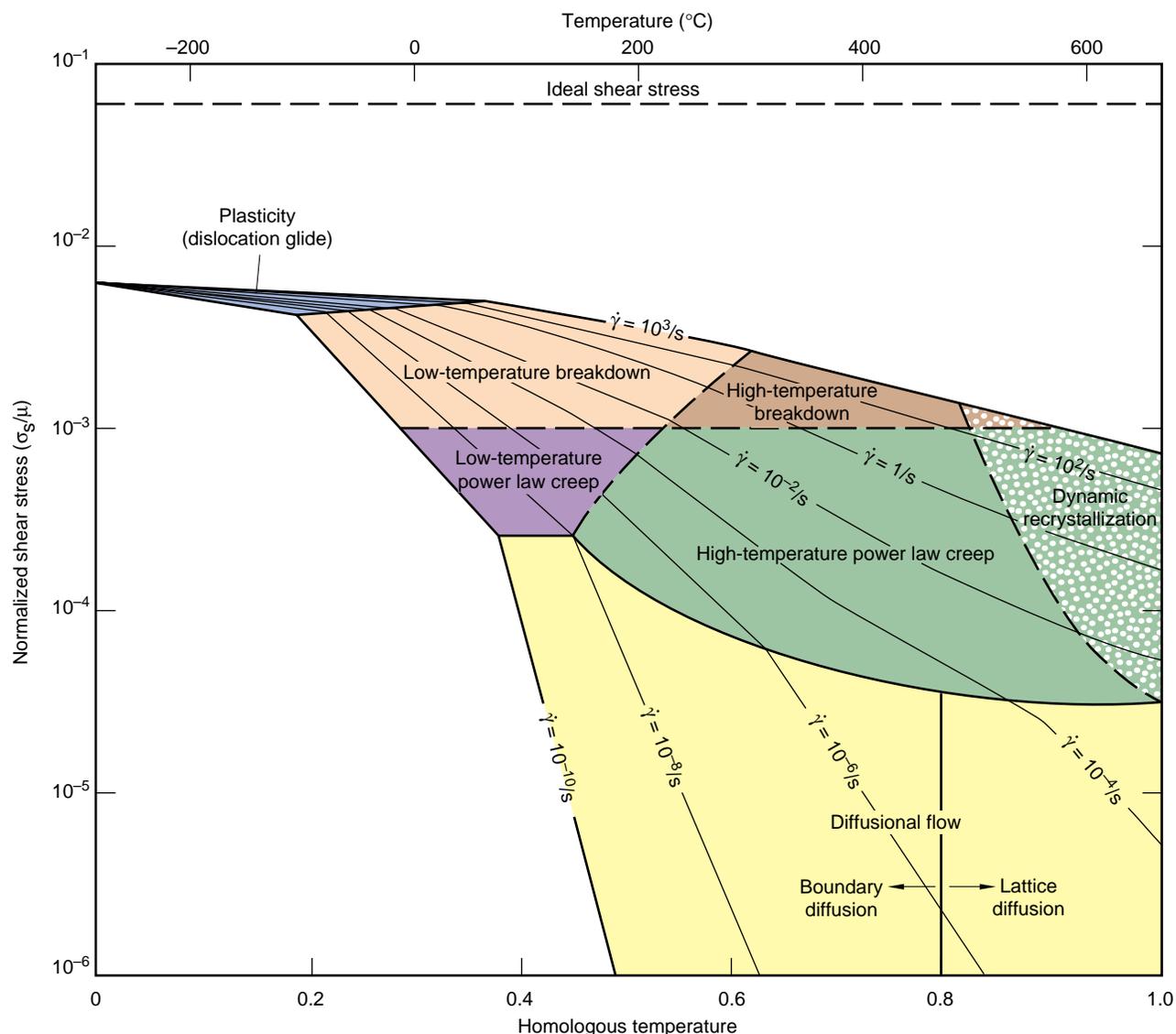
Figure 7. Map of Deformation Mechanisms for Pure Aluminum

The deformation-mechanism map for pure aluminum (10-μm grain size) was created by Frost and Ashby (1982). The different regions of flow (plasticity by dislocation glide, breakdown creep, power-law creep, and diffusional flow) correspond to the mechanisms shown in Figures 8 and 9. The region for dynamic recrystallization is indicated by the mottled area. The fine black lines represent the shear strain rate expected in these regions for a given normalized shear stress level and homologous temperature. For example, at $T/T_m = 0.4$ and a normalized stress of 3×10^{-3}, aluminum would deform in the low-temperature breakdown creep regime with a shear strain rate $\dot{\gamma}$ of 1/s. Note that there is very little rate sensitivity in the dislocation glide regime. For example, at $T/T_m = 0.2$, the normalized shear stress varies by as little as ~25% over 13 orders of magnitude of shear strain rate. Frost and Ashby also showed that there is only a mild dependence of dislocation glide on grain size. However, the other deformation regimes are a strong function of grain size. (This figure was adapted with permission from Michael F. Ashby.)

the dislocations multiply during slip, presenting increasing obstacles to the plastic flow and thereby increasing the flow strength, or instantaneous resistance to dislocation glide. This process, known as work hardening, can increase the yield strength of fcc metals several-

fold before the metals fail in a ductile manner (see Figure 1). Both δ-phase plutonium alloys and aluminum respond in this way during a tensile test—see Figure 2(a).

Alloying with solutes such as aluminum or gallium also introduces a

friction-like resistance to dislocation glide. These solute atoms represent weak obstacles for moving dislocations and therefore strengthen the fcc crystal only moderately. However, increased solute concentrations of aluminum or gallium do produce additional harden-
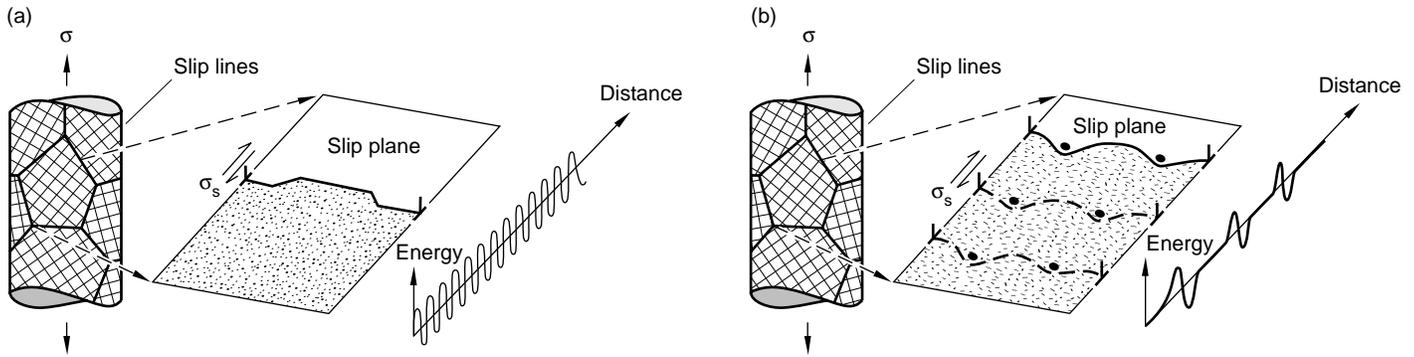
Figure 8. Plastic Flow at Low Homologous Temperatures

Plastic flow at low temperatures (T/T_m < 0.3) is controlled predominantly by dislocation glide in response to a shear stress (σ_s) on close-packed planes. Glide can be limited by the intrinsic lattice resistance (Peierls' stress) as shown in (a). This resistance is extremely low (<10^{-5} of the shear modulus) for most fcc metals at all temperatures and quite low for bcc and hcp metals at higher temperatures. The dislocation velocity is determined by the ability of the dislocation to nucleate and propagate kinks—the bends in the dislocation line shown in (a). This process becomes very difficult in bcc metals at temperatures less than a T/T_m of 0.15. Consequently, the yield stress of bcc metals rises sharply below these temperatures. Typically, the lattice resistance of lower-symmetry crystals varies substantially for different slip planes. (b) Plastic flow in fcc metals is controlled predominantly by the interaction of dislocations with discrete obstacles (other dislocations, point defects, solute atoms, grain boundaries, second-phase particles, and precipitates). For bcc and hcp metals, strengthening by discrete obstacles begins to overshadow strengthening resulting from the intrinsic lattice resistance as the temperature is increased. The slip lines shown schematically are surface offsets caused by the glide motion of hundreds of thousands of individual dislocations. (Reproduced courtesy of Michael F. Ashby.)

ing, as is observed in experiments. By introducing dispersed particles or second-phase precipitates, one can also strengthen fcc metals substantially. The amount of strengthening depends on the strength of the particle, its size, and the spacing—which will govern whether a dislocation can cut through the particle or has to bow around the particle. Generally, the stronger the particle and the finer the dispersion, the greater the strengthening. For example, large second-phase inclusions do very little to strengthen fcc metals since the dislocations do not develop an effective interference with such particles.

The low homologous temperature regime also favors deformation twinning, especially when the lattice resistance for dislocation glide becomes substantial as in bcc and hcp crystals at low temperatures. Twinning is sensitive to the sign of the shear stress whereas dislocation glide is not. Although little twinning was observed in α-plutonium at room temperature, we expect twinning to be a more-dominant deformation mode below room temperature.

As the homologous temperature is increased, atomistic processes other than dislocation glide and twinning begin to dominate—in particular, the coupled glide and climb of dislocations, the diffusive motion of individual atoms, and the sliding of grain boundaries to produce relative displacements of grains (involving diffusion and defect motion in the boundaries). Figure 9 illustrates several of these mechanisms as well as the process of dynamic recrystallization.

Under conditions of explosive or shock loading (typically at strain rates >10^6/second) dislocations can enter the "dislocation drag" regime, in which their velocity is limited by interaction with phonons or electrons. The drag-controlled regime is poorly understood for most metals, including plutonium and its alloys.

This very brief overview of the kinetics of plastic flow demonstrates that atomistic processes control the macroscopic shear-strain rate and that microstructure plays a predominant role. For more complete treatments, refer to the extensive work of Frost and Ashby (1982) and Kocks et al. (1975).

Anomalous Rate-Dependent Deformation in α-Plutonium

The mechanical strength of polycrystalline unalloyed plutonium in the α- and β-phase depends strongly on temperature, as shown in Figure 2(b). Merz and Nelson (1970) showed that polycrystalline α-plutonium is also much more sensitive to strain rate close to room temperature than first expected (see Figure 10a). Their results provided the first definitive evidence that deformation mechanisms, in addition to slip by dislocation glide, come into play at the higher end of the α-phase temperature range and in the β-phase range, that is, at apparently low homologous temperatures.

Grain-boundary sliding, for example, was shown to play a prominent role in the deformation of fine-grained α- and

(a) Triple point of grain boundary
σ
Dislocations move by glide plus climb
Single grain

(b) σ
Dislocations move mainly by climb
Lattice diff.
Core diff.
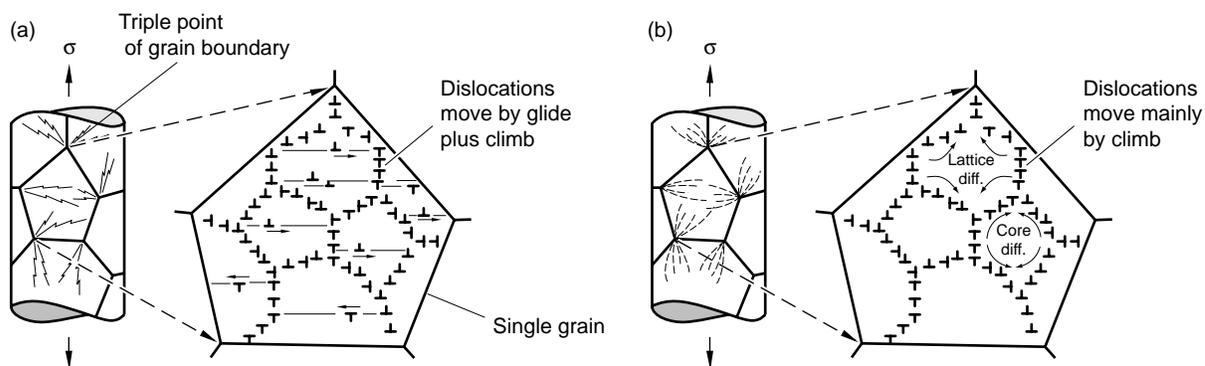
Figure 9. Plastic Flow at High Homologous Temperatures

Plastic flow at elevated temperatures (T/T_m > 0.3) is very much rate-dependent and is typically referred to as creep. (a) The regime in which dislocation glide plus climb dominates is prevalent at relatively high stresses—a region known as power-law breakdown. The overall strain rate is controlled primarily by dislocation glide. Cells or subgrains begin to form within the grains because the temperature is high enough that the stored energy resulting from dislocation buildup can be reduced if the dislocations organize themselves into cell or subgrain boundaries. Climb of edge **dislocations helps to organize and align the dislocations within these boundaries. The bundles of slip lines at the triple points of grain boundaries here and in (b) suggest strongly inhomogeneous deformation. (b) At lower stresses (the power-law regime), creep is controlled mainly by climb. If a gliding dislocation is held up at an obstacle, a little climb may release it, allowing it to move on to the next obstacle. Although the glide step is responsible for most of the accumulated deformation, the climb step determines the average velocity. Since climb is more** **prevalent than in (a), the dislocations within the cells or subgrains are more aligned. Also, the strongly inhomogeneous deformation at the triple points is accommodated by slip and climb, so slip traces would appear more rounded. At T/T_m >0.6, climb is generally controlled by lattice diffusion. At lower temperatures, experimental results show that accelerated diffusion at the dislocation core appears to be rate controlling. The arrows in the right-hand sketch of (b) indicate the directions of atom movement resulting from lattice and core diffusion.**

(c) σ
Boundary diffusion
Lattice diffusion

(d) σ
Old deformed grains
New grains
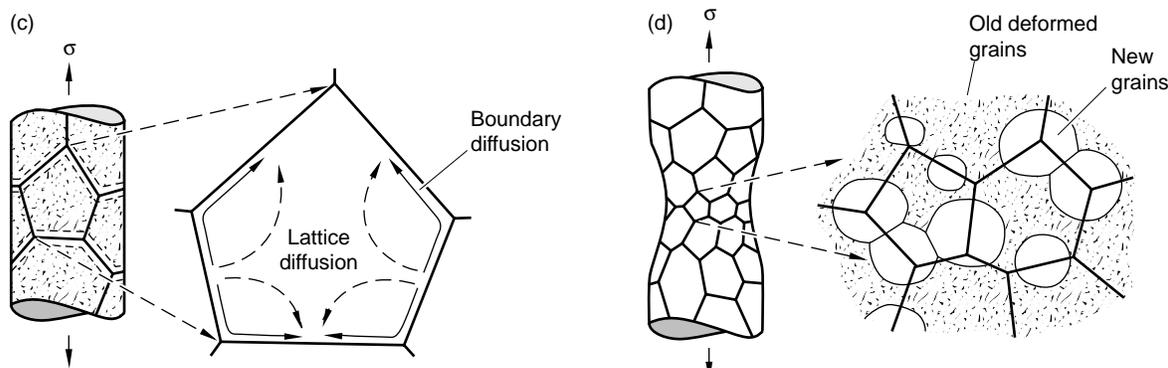
(c) Deformation by atomic diffusional flow is illustrated. Shear stresses can induce a change in the chemical potential of atoms at the grain surfaces in polycrystals, giving rise to the diffusional flow illustrated. The chemical potentials on some grain surfaces are affected more than others, depending on grain orientation to the stress axis. The left-hand sketch is shaded to accent those areas of the grain surface that are favorably oriented to trigger diffusional transport of atoms. Such flow by diffusional transport through and around grains, coupled with sliding displacements in the plane of the **boundaries, leads to strain. The clear areas near grain boundaries are meant to denote those surfaces at which the diffused atoms accumulate. As in (b), strain rates are controlled by lattice diffusion at higher temperatures and by grain-boundary diffusion (instead of dislocation core diffusion) at lower temperatures. This deformation mechanism becomes more important for very fine grained polycrystals, whose grain-boundary surface areas are very large. (d) At T/T_m 0.6, creep deformation may also be accompanied by repeated waves of recrystallization, a process called dynamic recrystallization,** **which is shown here. This process occurs first by enough accumulation of lattice damage from primary creep (the mottled areas in the right-hand sketch represent stored energy resulting from dislocation interaction and multiplication). The next step is recrystallization (generation of new, relatively strain-free grains with a greatly reduced dislocation density) to relieve the buildup in strain energy during deformation. This cycle is then repeated numerous times, depending on temperature and deformation strain rate.**
(This figure was reproduced courtesy of Michael F. Ashby.)
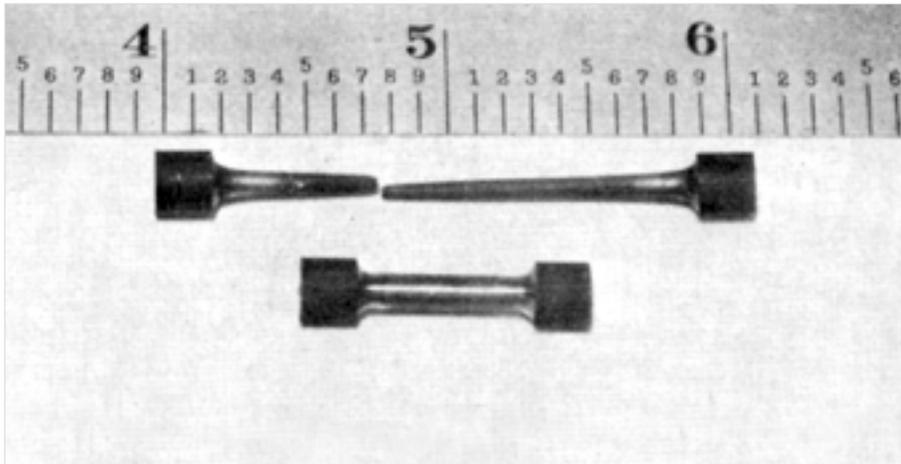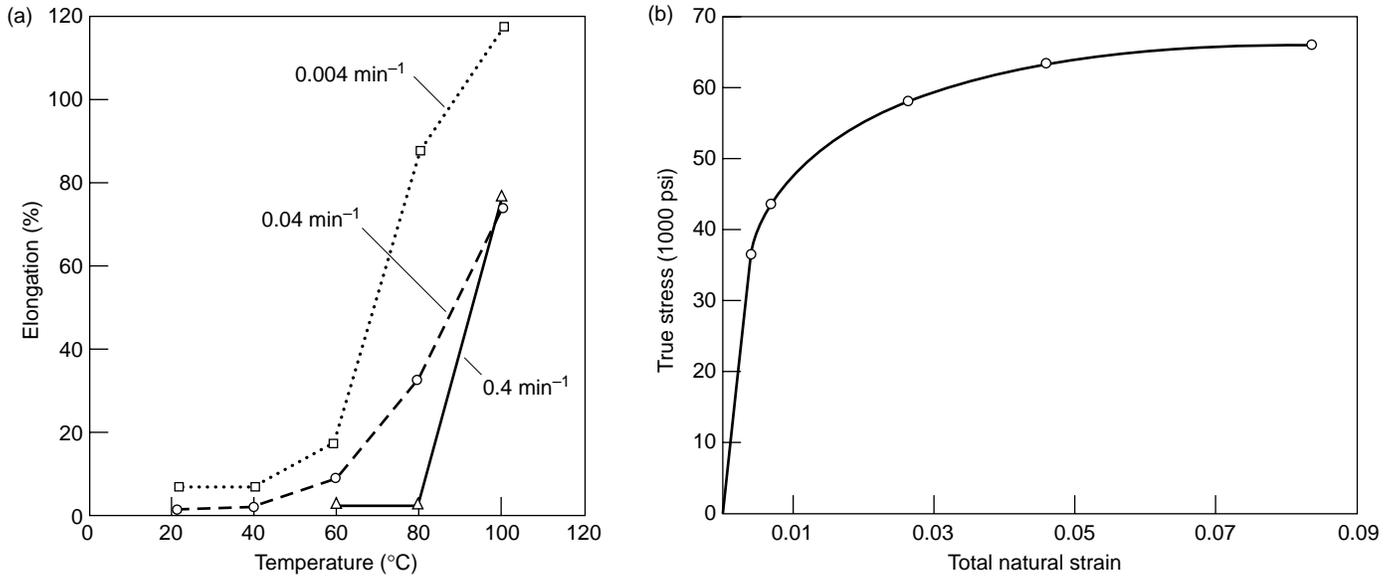
Figure 10. Tensile Test Results for Extruded Polycrystalline α-Plutonium
(a) Tensile test results (Merz 1973) for extruded polycrystalline α-plutonium show how ductility (as measured by percent elongation in tension) changes with temperature and testing speed (strain rate). (b) Tensile stress-strain curve for fine-grained extruded α-plutonium tested at a strain rate of 0.7×10^{-4}/s at room temperature shows substantial ductility. (c) A sample of the same α-plutonium was subjected (Merz 1971) to a tensile stress-strain test at 108°C, during which it was strained to 218% its original length.

β-plutonium. Such sliding involves shear at the grain boundaries, translation of grains, some dislocation glide and climb, and diffusional flow (shown schematically in Figure 8) so that grains can accomplish a shape change. In most metals and alloys, grain-boundary sliding and diffusional flow become predominant deformation modes if strain rates are low, grains are very small, and temperatures are above half the melting point. These mechanisms mostly rearrange the grains while causing very little work-hardening or change in grain shape. Such mechanisms can lead to "superplastic" behavior, that is, elongations by several hundred percent. This behavior has been observed in fine-grained (micrometer-size) lead-thallium alloys at room temperature and aluminum alloys tested above half their melting points.

Merz (1971, 1973) prepared polycrystalline α-plutonium extruded and recrystallized to yield very fine grains of 1 to 3 micrometers in diameter compared to typical grain sizes of 20 to 50 micrometers. Pulled in tension at room temperature, these samples produced a surprising elongation of 8 percent before the material failed in a ductile manner—see Figure 10(b). At higher temperature (108°C), this material showed amazing ductility, extending over twice its original length before failing. We should note here that, once grain-boundary sliding replaces dislocation glide as the dominant mechanism of deformation, the relationship between strength and grain size reverses. For slip by dislocation glide, smaller grains increase the strength because the grain boundaries are discrete obstacles to dislocation glide, whereas for grain boundary sliding, small grains make sliding easier (because there is more grain-boundary surface area) and lower the strength. However, at high strain rates, small grains strengthen because there is insufficient time for the diffusional processes involved in grain-boundary sliding to take place.

Merz and Nelson (1970) also showed that dynamic recrystallization—shown schematically in Figure 9(d)—can occur in α-plutonium concurrently with grain-boundary sliding.

Recrystallization allows a deformed material to lower its energy by rearranging its defects (developed during deformation) so as to create entirely new grains. In α-plutonium, the deformation leading to dynamic recrystallization must be introduced in a very confined manner (for example, by extrusion) so as not to fracture the material in tension. Merz and Nelson extruded α-plutonium in the upper temperature region of stability and found that as little as 3 to 14 percent strain will cause dynamic recrystallization. Merz's deformation map (Figure 11) shows that both slip (dislocation glide) and grain-boundary sliding (accompanied by diffusional flow) play prominent roles in the deformation of α-plutonium. In addition, dynamic recrystallization was found to occur even at room temperature if very large deformation was applied. The map shown in Figure 11 is not based on the same rigorous framework developed by Frost and Ashby (Figure 9). Nevertheless, it is useful in helping us examine the deformation of α-plutonium.

In the β-phase, the conditions that favor grain-boundary sliding (low strain rate, high temperatures, and small grain size) have even more dramatic effects. Merz showed that, if the β-phase is formed from the α-phase (that is, by cooling first to the α-phase and then reheating into the β-field), it has a fine grain size of 5 micrometers and is superplastic, extending up to seven times its original length. In contrast, β-plutonium formed from γ-plutonium has a grain size of 50 to 500 micrometers and elongates by only 5 percent before it fails.

The experimental results we have shown demonstrate that, under the right conditions of temperature, strain rate, and microstructure, the α- and β-phase of plutonium can be remarkably ductile whereas monoclinic structures are typically brittle. In fact, one can achieve superplastic behavior. Finding these surprising rate effects and large plastic deformations in plutonium near room temperature is surprising until one real-
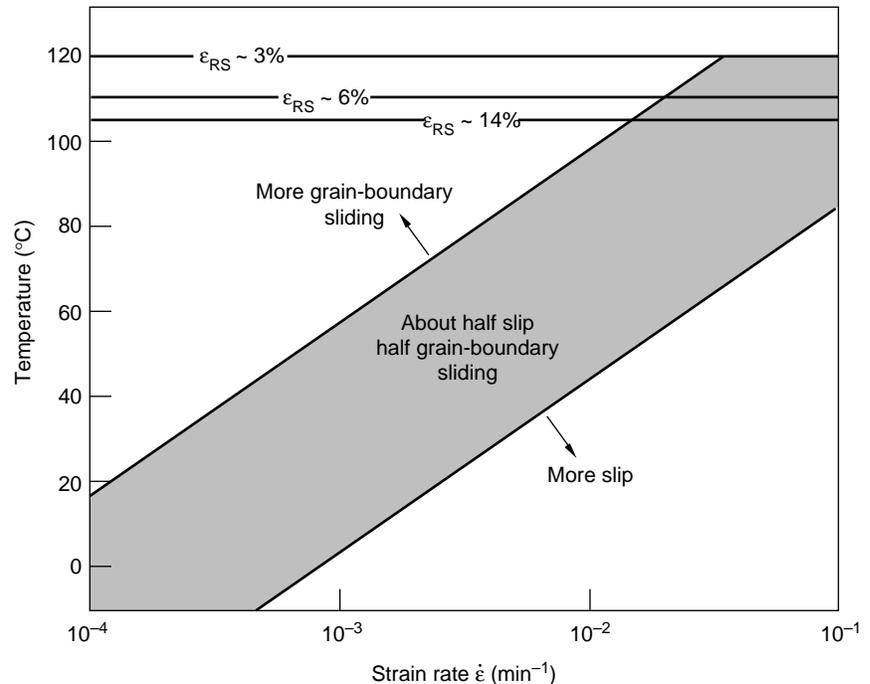
Figure 11. A Simplified Deformation Map for α-Plutonium
A simplified deformation map for α-plutonium within the α-phase temperature range and at moderate strain rates was proposed by Merz (unpublished research at Pacific Northwest Laboratory). Both slip by dislocation glide and grain-boundary sliding are prevalent. Higher temperature, lower strain rates, and smaller grain sizes favor grain-boundary sliding. The strain required for dynamic recrystallization (ε_{RS}) is shown for three temperatures.

izes that the value of the effective homologous temperature for α-plutonium at room temperature is actually 0.53, not 0.32 as calculated on the basis of the actual melting point of 913 kelvins (see the article "Plutonium and Its Alloys" on page 290). Therefore, the α-plutonium results are consistent with the results for other metals that show grain-boundary sliding, diffusional flow, and dynamic recrystallization to occur only above half the melting point.

Stress-Assisted or Deformation-Induced Transformation. Another fascinating aspect of mechanical behavior in plutonium and its alloys is the strong interplay between stress (or deformation) and transformation. Let's look first where we would least expect it—in α-plutonium. Under increased pressure, the α-phase maintains its well-known

room-temperature stability within a wide range of temperatures. However, we found a hint of a new instability when we examined the fracture surface of typical polycrystalline α-plutonium (50-micrometer grain size). The sample had exhibited very little plastic strain (< 0.1 percent) when fractured in tension at room temperature. The tensile fracture looked macroscopically brittle, and the sample failed in a perpendicular direction relative to the applied stress, as expected. We were astonished (so much so that we thought we had mixed up the samples) when an examination of the fracture surface by electron microscopy showed ductile dimples—Figure 12(a). Although the dimples were very shallow, thereby indicating limited plastic flow, they were unmistakably ductile.

(a)

(b)

(c)

(d)
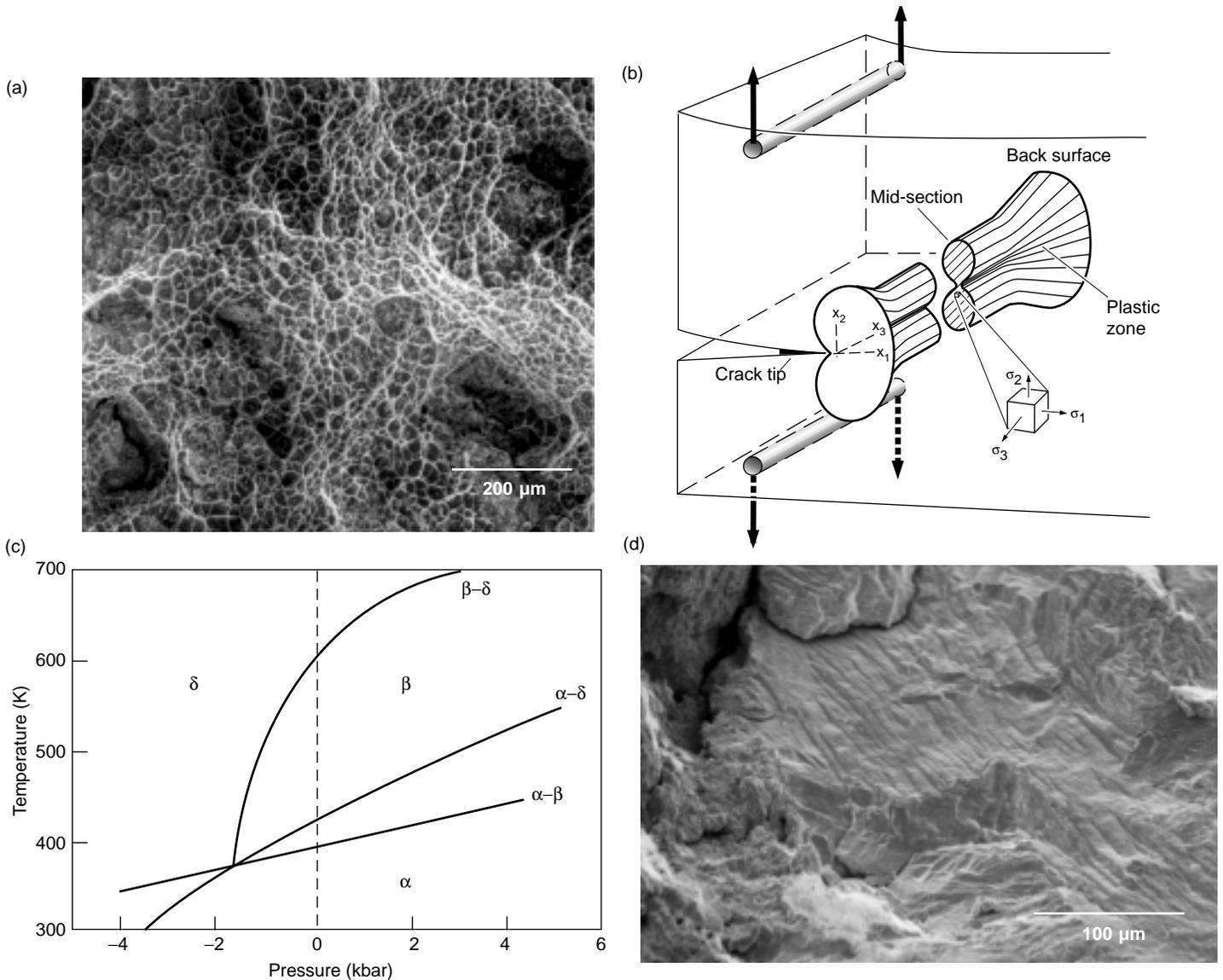
Figure 12. Evidence for α to δ Tansformation during Hydrostatic Tension

(a) Typical polycrystalline α-plutonium tested in tension at room temperature fails in a macroscopically brittle manner with little energy absorption but with evidence of microscopic ductility. The "ductile-dimple" fracture surface in the micrograph looks very much like that of a peanut butter sandwich that has been pulled apart. This image was taken with a scanning electron microscope. (b) This schematic shows how the stress field at the tip of an advancing crack creates a state of triaxial tension that can reach levels as high as three times the applied uniaxial stress. (c) Robert Mulford of Los Alamos extended the metastable phase boundaries of the δ- to α-phase field to hydrostatic tension (negative pressure) and showed (unpublished work) that, at room temperature, the α-phase becomes unstable and transforms to the δ-phase at ~ –3.6 kbar (or 365 MPa). (d) The surface of a macroscopically brittle α-plutonium sample fractured in torsion (shear) shows cleavage facets indicative of microscopically brittle fracture. There is no hydrostatic tension in shear fracture, and we find a typical brittle-fracture surface with no evidence of the α to δ transformation found in (a).

The connected neptunium-plutonium-americium phase diagram (see Figure 18 in the article "Plutonium and Its Alloys" on page 290) provides a clue for solving this puzzle. The addition of neptunium increases the stability of the α-phase, whereas americium expands the δ-phase field and makes the

α-phase unstable. Therefore, adding neptunium to plutonium mimics the application of hydrostatic pressure, and it is reasonable to assume that adding americium resembles applying "negative" pressure (hydrostatic tension). Therefore, applying hydrostatic tension may promote the transformation from

α to δ, but hydrostatic tension is difficult to achieve—except at the stress field near a crack tip, as shown in Figure 12(b). Our initial suggestion that the α-phase transforms to the δ-phase just ahead of the crack tip, as the brittle crack propagates, was found to be quite plausible in the more rigorous

analysis reported by Adler et al. (1992). Little energy is absorbed in the δ-layer as it fails by ductile fracture because the δ-layer is very shallow, resulting in a macroscopically brittle-looking fracture. Moreover, once the crack tip passes, the hydrostatic tension disappears, and the surface transforms back to α-plutonium, destroying the evidence. Indeed, examination of the fractured surface showed only α-plutonium. One indirect check of this hypothesis is to fracture α-plutonium in torsion, which produces no hydrostatic tension. The brittle cleavage features of the scanning electron micrograph of a torsion sample shown in Figure 12(c) support our hypothesis.

We also examined the likelihood of hydrostatic-tension-induced α to δ transformation by extrapolating the plutonium allotropic phase boundaries of the pressure-temperature diagram backward to negative pressure. In unpublished work, Robert Mulford of Los Alamos estimated that, at room temperature, α-plutonium would transform to the δ-phase at 3.6 kilobar (365 megapascals), as shown in Figure 12(d). The component of hydrostatic tensile stress at a crack tip can reach three times the applied tensile stress. Because the applied stress is limited by the tensile strength of the material (350 to 500 megapascals for α-plutonium), it is quite likely that the hydrostatic-tension component at the crack tip exceeds the projected 365 megapascals required to transform α- to δ-plutonium. Interestingly, the band structure calculations of Wills and Eriksson (see the article "Actinide Ground-State Properties" on page 128) predict that, in the absence of applied stress, the free surface of α-plutonium also transforms to δ-plutonium over a very thin surface layer.

We have also seen deformation-induced transformation of α to δ in as-cast plutonium-aluminum (Pu-Al) and Pu-Ga δ-phase alloys that contained significant amounts of retained α-phase because of their cored (segregated) microstructures. When the composite of

α- and δ-phase was fractured in tension, regions of the α-phase transformed, creating thin spikes of δ-phase (shown in Figure 13). The transformation and the accompanying plastic deformation blunted the crack tip and provided additional fracture resistance. Taken together, these results provide undisputable evidence that, given sufficient hydrostatic tension, the α-phase will transform to the δ-phase and greatly influence the resulting mechanical behavior.

Conversely, it is well known that δ-plutonium alloys collapse easily to an α-phase under hydrostatic pressure via a martensitic phase transformation (refer to the article "Plutonium and Its Alloys"). In most materials, shear stresses and plastic deformation, as opposed to hydrostatic pressure, are most effective in promoting martensitic transformations, but the δ to α transformation in plutonium alloys is governed primarily by the hydrostatic-stress component. For example, when Pu–2 at. % Al is deformed at room temperature in uniaxial compression, it does not transform to α even at strains as large as 0.7. The strength of the δ-phase, or the maximum hydrostatic pressure (1/3 of the uniaxial compressive stress), at these large strains is only ~50 megapascals, whereas the hydrostatic pressure required to transform this alloy at room temperature is closer to 250 megapascals. Robbins and coworkers at Lawrence Livermore National Laboratory and we, at Los Alamos, have also deformed Pu-Ga alloys to very large strains (on the order of 10—that is, by 1000 percent) in torsion (pure shear and no compressive component) without finding any deformation-induced transformation from δ to α. On the other hand, during cold-rolling plutonium billets into thin sheet, it is possible to partially transform the δ- to the α-phase because a significant hydrostatic-pressure component exists during rolling and the strength of the δ-phase is elevated significantly by work hardening. The δ to α transformation is facilitated by lowering the temperature or by lowering

the solute concentration of alloys. For example, δ-phase Pu–3.4 at. % Ga alloys will not transform to α in uniaxial compression at room temperature, but will do so readily at 77 kelvins.

It appears that hydrostatic pressure is the most effective agent of a stress-assisted martensitic transformation from δ to α, and plastic deformation has, at most, a minimal role in providing more favorable nucleation sites for that transformation. Hence, instead of shear stress or deformation dominating the transformation behavior, as it does in most ferrous alloys, hydrostatic stress dominates in plutonium. If the hydrostatic stress is tensile, the α to δ transformation is favored; if it is compressive, the reverse is favored.

To conclude, we comment just briefly on the strengthening of weak δ-phase plutonium alloys. In this case, the stress-induced δ to α transformation provides an even more effective strengthening mechanism than work hardening because it distributes a network of hard α-phase platelets throughout the parent δ-phase. Also, alloying additions—such as aluminum, gallium, silicon, scandium, cerium, and americium—strengthen the δ-phase moderately. Other elements that do not dissolve in the δ-phase are quite ineffective. Elements such as carbon, oxygen, nitrogen, and hydrogen form relatively large (micrometer-size) inclusions that do not interfere with dislocation glide. Likewise, the eutectic-forming elements—iron, nickel, and manganese—form very large inclusions (often tens of micrometers in size) and also tend to be ineffective strengtheners. Carbide, oxide, and nitride inclusions are very brittle and will act as nucleation sites for fracture. Low-melting eutectic inclusions—for example, of the plutonium-iron compound Pu_6Fe—bond poorly with the δ-phase and will therefore also nucleate fracture. Fortunately, δ-phase alloys are sufficiently ductile that a moderate concentration of such impurities does not seriously limit their fracture resistance.

(a)

Away from crack tip

At crack tip

(b)

20 µm

5 µm
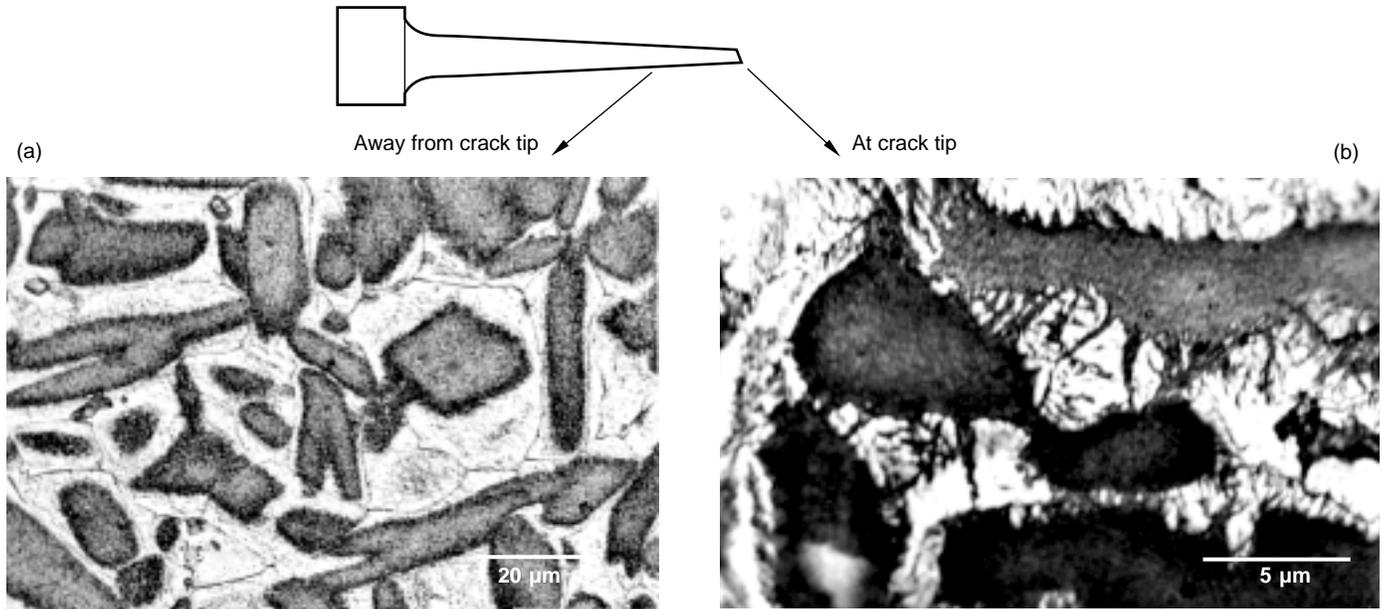
Figure 13. Further Evidence for α to δ Transformation during Hydrostatic Tension
(a) The metallographic cross-section of an as-cast Pu-Ga alloy consists of two phases because of gallium segregation during cool-
ing: a continuous α-phase that etches light (the thin, dark lines inside the light areas are remnants of high-temperature ε-grains) and
islands of δ-phase that etch dark. This structure represents the starting material and is representative of the tested sample away
from the tensile-fracture area. (b) The cross section very near the fracture shows dark bands extending through the light α-phase re-
gions. These bands are δ-spikes transformed from α near the crack tip. The areas of the sample more than a few millimeters from
the fracture showed no transformation product.

Concluding Remarks

The fascinating examples discussed in this article are intended to demonstrate the richness and complexity of mechanical behavior in plutonium and its alloys and to whet the appetites of future researchers. The Frost-Ashby map introduced in Figure 7 provides an excellent tool for identifying the crucial ingredients necessary for a fundamental understanding of the mechanical behavior of α-plutonium and δ-phase plutonium alloys. We know very little about the fundamental properties of dislocations in the monoclinic crystal structure. For example, does the unusual electronic structure of α-plutonium, which manifests itself in eight distinct atomic positions in the lattice, affect the nature of the lattice resistance or other characteristics of dislocations? Does the yield strength at absolute zero temperature approach an appreciable fraction of the

theoretical shear strength because of increased lattice resistance at low temperatures? Does twinning play a dominant role in the deformation of polycrystalline α-plutonium at low temperatures or high strain rates? What is the role of crystallographic texture in the deformation of α-plutonium, and why is it so easy to induce significant texture through the β to α transformation?

A detailed construction of a deformation-mechanisms map would help to quantitatively determine the interplay between dislocation glide and grain-boundary sliding found by Merz and Nelson (1970). And a better understanding of the stress-induced α to δ transformation in α-plutonium or in α + δ alloys would determine if such transformations absorb sufficient energy to greatly improve fracture resistance. We should emphasize that single crystals are very important for most of these fundamental studies, including determining elastic constants over a

wide range of temperatures (see the article "Elasticity, Entropy, and Phase Stability of Plutonium" on page 208).

For δ-phase alloys, we need a quantitative description of the deformation-mechanisms map, which would determine, for example, whether the Mechanical Threshold Strength Model developed at Los Alamos by Follansbee and Kocks (1988) describes the behavior of these alloys in the dislocation-glide regime. Whereas the map for pure aluminum (Figure 7) shows that steady-state strain rates change very little with stress and temperature in this regime, we expect the stress-induced δ to α transformation in plutonium alloys at low temperature and high strain rates to cause significant strengthening under transient loading conditions. In fact, the transformation behavior will introduce new variables into the deformation-mechanisms map, namely, the sign of the applied stress and the effect of the hydrostatic-stress

component. These are typically neglected for dislocation glide because glide results from the shear stress—that is, it depends very little on the hydrostatic stress and not at all on the sign of the shear stress. These effects will also be important in the shock-loading regime, in which the applied stress produces large hydrostatic stresses. Consequently, pressure-induced transformations may dominate the mechanical response. In addition, dislocation drag, which results from the interactions of dislocations with phonons or electrons (these interactions are expected to dominate in the shock-loading regime), remains virtually unexplored for plutonium. These are areas in which the mechanical behavior of δ-phase plutonium alloys may differ greatly from that of their more stable fcc cousins.

We must also develop a much better fundamental understanding of the effects of self-irradiation damage on the mechanical behavior of α-plutonium and δ-phase plutonium alloys. At low temperatures, both materials undergo substantial lattice damage, resulting in loss of crystallinity, or amorphization (see the article "Aging of Plutonium and Its Alloys" on page 238). At ambient temperature, most lattice damage is annealed out. We do not know how the residual damage affects phase stability, diffusion, and dislocation dynamics. In addition, we know that, as little as 100 atomic parts per million (ppm) of helium in stainless steel cause dramatic embrittlement. In plutonium, roughly 40 atomic ppm of helium per year are generated internally. Although we have not observed plutonium or its alloys "crumble" even after decades of storage, we do not know if helium degrades any of the mechanical properties. In other words, we have very little understanding of the effects of aging on mechanical behavior. In all cases, better materials models with realistic interatomic potentials are required to help guide much-needed experimental work.

The fundamental work we have outlined in this article will provide a much better foundation for understanding the engineering response of plutonium and its alloys and will allow us to deal with the difficult job of predicting or extending the lifetime of plutonium in weapons or in storage. ∎

Acknowledgments

Further Reading

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