Los Alamos researchers Deniece Korzekwa and Phil Tubesing position a cylindrical graphite funnel over a graphite mold used to cast pieces of uranium alloy. Proper casting helps produce alloy pieces that age gracefully. The upper background shows regions of high niobium content (green) and low niobium content (blue) that make up the complex microstructure of uranium-niobium alloy. The lower background shows a polished, pure uranium sample exposed to air overnight. The colors are produced by the interference of light in the oxide films that form on the microcrystals.

Aging and Deformation of Uranium-Niobium Alloys

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One of the major goals of stockpile stewardship is to ensure that weapons in the nation's nuclear stockpile will perform as designed—even as the weapons age. To pursue this goal, we studied the crystal structure of uranium-niobium alloys. Such studies provide insight into how the alloys age and deform under stress. For example, we determined that one of these alloys deforms under stress as shape-memory alloys do, that is, mainly by reorienting its crystalline "twins." This result can be used in computer models to more accurately predict part performance. Our next step will be to measure changes in the crystal structures of aged alloys as they are subjected to stress and elevated temperatures.

As the nation's nuclear stockpile ages, there are concerns that the properties of the materials in the weapons could degrade to values outside acceptable design limits. Depending on the application, values for properties such as strength, ductility, and hardness may be specified in the design, but these values can change with time. The causes of aging are manifold and inexorable; they include corrosion, oxidation, chemical reactions, radiation damage, and changes in crystal structure. The last of these mechanisms—in which atoms adopt increasingly lower energy states due to thermodynamic considerations—is particularly important for a class of uranium-niobium alloys relevant to the nation's nuclear stockpile. How the crystal structures of these alloys change as a function of composition, aging, and stress is the subject of this article.

Uranium-Niobium Microstructures

Uranium-6 weight% (wt%) niobium (U-6Nb) has several properties that make it desirable for weapon applications. Among them are corrosion resistance and the ability to be heat-treated to obtain strength–ductility combinations that facilitate fabrication. When U-6Nb enters the stockpile, it is thermodynamically metastable, with a majority phase called α'' (a monoclinic distortion of the orthorhombic α-uranium phase characteristic of pure uranium) that maintains a significant supersaturation of niobium owing to the diffusionless martensitic mechanism intrinsic to its formation. The microstructure also exhibits remnants of segregation patterns that develop when the alloy is cast, giving compositional variations at length scales of approximately 100 micrometers of up to +/–2 wt% niobium about the nominal 6 wt% niobium mean value. This variability in composition and microstructure and its effects on hardness can be seen in Figure 1.

Despite its comparatively complicated microstructure, the alloy's mechanical properties are appropriate for the application at the time of fabrication and insertion into the stockpile—the problem is that the alloy is metastable. The metastability is in the form of niobium supersaturation that is relieved through a diffusion-controlled phase reaction, in which a body-centered-cubic γ_2 phase precipitates. That phase contains more than 50 wt% niobium. The precipitation depletes the remaining matrix phase of niobium, transforming the matrix to α-uranium, which is susceptible to corrosion. Moreover, even before the decomposition reaction reaches a final $\alpha + \gamma_2$ equilibrium,

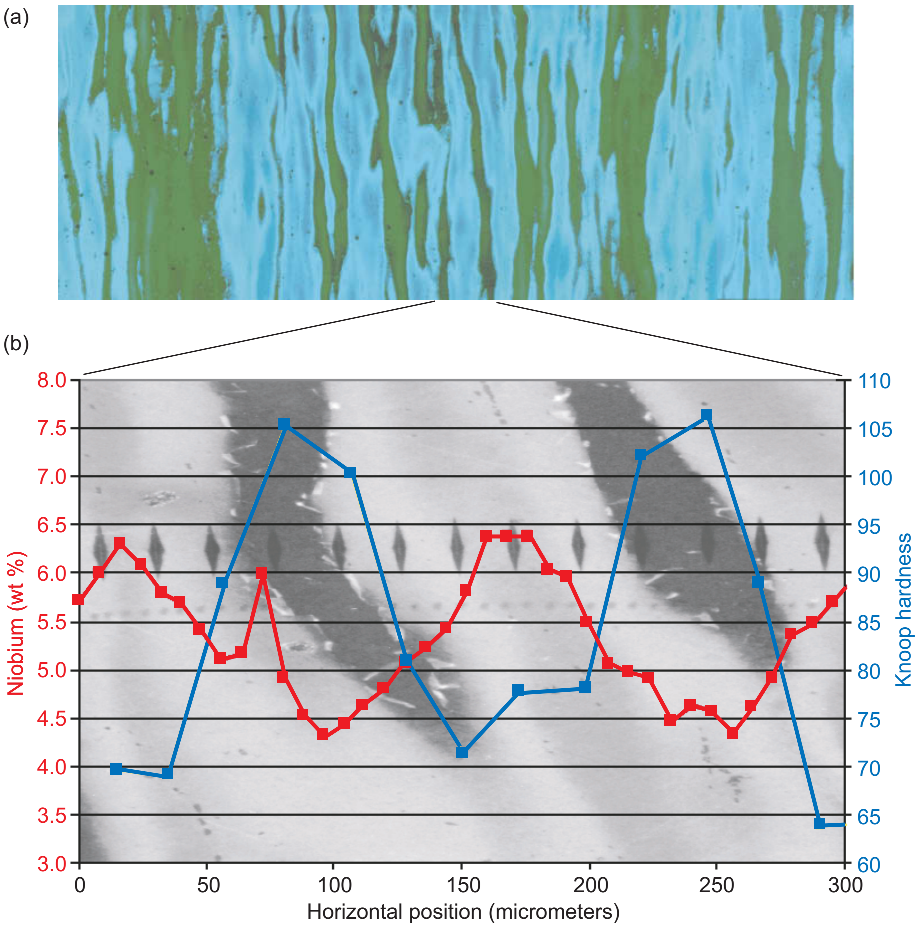

Figure 1. Microstructure and Banding in U-6Nb
(a) The light microscope image reveals the edges of pancake-shaped bands, with blue and green indicating opposite extremes of compositional variation. (b) Two of these bands are magnified in this image, and the composition and hardness traces are superimposed.

other changes occur. For example, the strength increases at the expense of reduced ductility, producing a material that is brittle and unable to deform without cracking. Figure 2 shows the effects of artificial aging at a temperature of 250ºC: Aged material exhibits much greater strength but little or no ductility compared with the as-quenched state of the material.

Is Aging a Cause for Concern?

At ambient temperature, the diffusion of niobium is slow—typically taking years to occur—but whether the diffusion is still rapid enough to cause concern over the decades that make up the anticipated lifetime of a weapon is unclear. Furthermore, at the upper extreme of compositional variation (regions with >6.5 wt% niobium), another metastable martensitic phase, tetragonal γ^0, can exist. In addition to being stronger than the α'' phase, kinetics studies suggest that γ^0 ages faster than α'' (Eckelmeyer and Thoma 2002), making it possible that premature embrittlement of pancake-shaped regions of high niobium content could occur.

Clearly, an understanding of the time scales and mechanical implications of the precipitations that take place in uranium-niobium alloy is important to ensure that the alloy's properties remain within design specifications even after decades in the stockpile. Since precipitation is a thermally activated process, exposing the material to elevated temperatures provides one way to accelerate aging. Because of the compositional banding and the likelihood of differential aging rates, a key question is how the aging rate is related to the local niobium content, which varies from 4 to 8 wt%.

Of equal importance is the quantitative relationship between precipitation and mechanical properties. The mechanical response of uranium-niobium alloy (Figure 2) exhibits a relatively unusual double-yielding phenomenon that is symptomatic of the special crystalline mechanisms (occurring in relatively few alloys) that account for plastic deformation. As shown below, these mechanisms prove to be composition dependent and introduce further uncertainty into the question of how aging affects function. At present, there is no rigorous criterion that defines property values beyond which a component will no longer perform its intended function. Further research on the crystallography of the components is required to scientifically inform the development and application of such a criterion.

Why Use Neutrons?

"Engineering performance" is generally defined in terms of bulk properties, but bulk properties are determined by microstructural effects. Thus, as we move from empirical to fundamental models of constitutive behavior, the importance of microstructural evolution during aging and concomitant changes in mechanical properties has been increasingly recognized. Phase, texture, and the

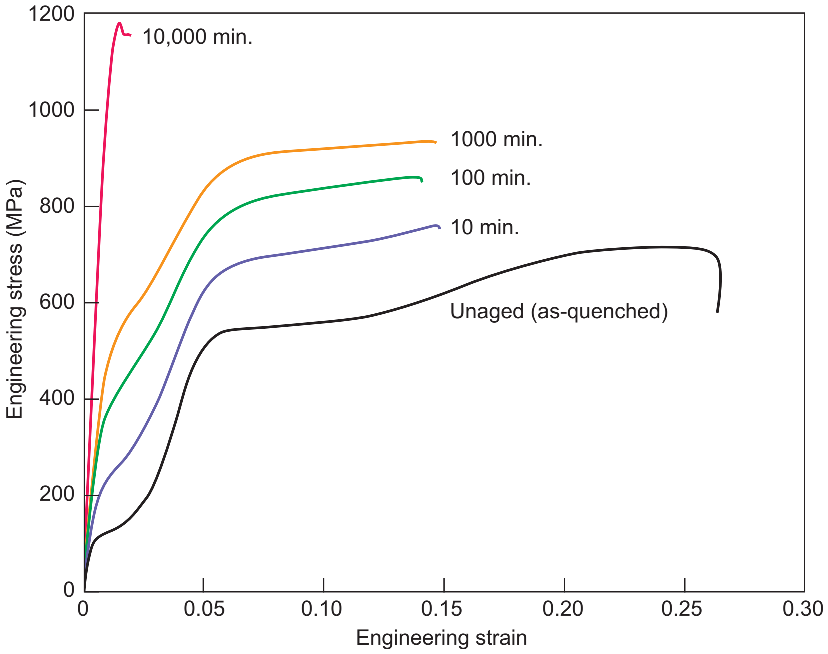

Figure 2. Tensile Stress–Strain Response of U-5.5 wt% Nb (Unbanded) as a Function of Artificial-Aging Time at 250ºC
The tests were performed at room temperature after the alloy had been aged at 250ºC. As the aging time increases, the stress required to deform the material increases, while the ductility decreases to almost zero for the 10,000-minute-aged material.

Figure 3. Interior of the SMARTS Experimental Cave at LANSCE
The 250-kN load frame with the 1800ºC furnace is mounted in front of the detector panel on the left.

partitioning of strain between different elements of the microstructure are all relevant. To explore their effects, conventional x-ray diffraction has been used for many years to study surfaces, but bulk and in situ measurements are uniquely suited to neutron diffraction. X-rays and electrons penetrate uranium to less than 1 micrometer, whereas neutrons penetrate it to more than 1 centimeter. The larger penetration depth of neutrons provides a key advantage in studying uranium alloys, whose propensity for surface oxidation and mechanical damage makes one uncertain whether surface-sensitive x-ray measurements represent the bulk. In the last few years, two new difractometers have been commissioned at the Los Alamos Neutron Science Center (LANSCE), SMARTS (Figure 3) and HIPPO. These instruments permit studies of bulk phase, microstructural, and strain response during aging or loading. The results identify the phases and deformation modes and complement conventional characterization by optical and electron microscopy, as well as measurements of heat capacity, electrical resistivity, and dilatometry.

Phase Evolution during Aging

To ensure that trends in martensite transition temperatures and lattice constants could be distinguished by neutron diffraction, a series of 41 compositionally homogeneous uranium-niobium alloys in 0.25 wt% niobium increments were prepared. Figure 4 shows short sections from the neutron diffraction spectra used to identify the phases present at niobium concentrations of 0 to 10 wt%. These data characterize the "baseline" compositions of unaged material. The next step was to evaluate the responses of different compositions at temperatures between 100°C and 300ºC. Over this temperature range, measurable precipitation

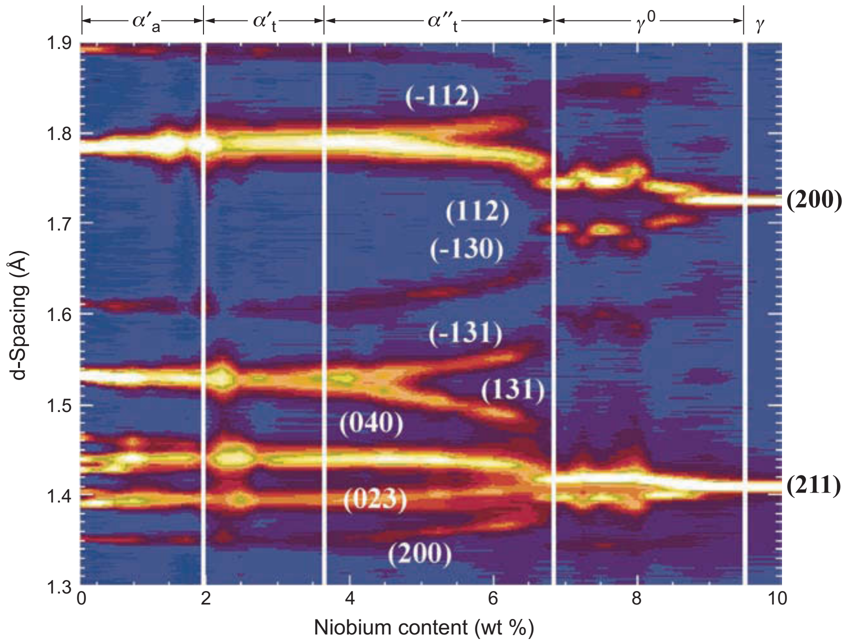

Figure 4. Uranium-Niobium Neutron Diffraction Patterns (1.3 to 1.9 Å)
These diffraction patterns are plotted against niobium content. The crystallographic (hkl) planes for the different reflections are labeled. The designations of the different phases are listed above the graph.

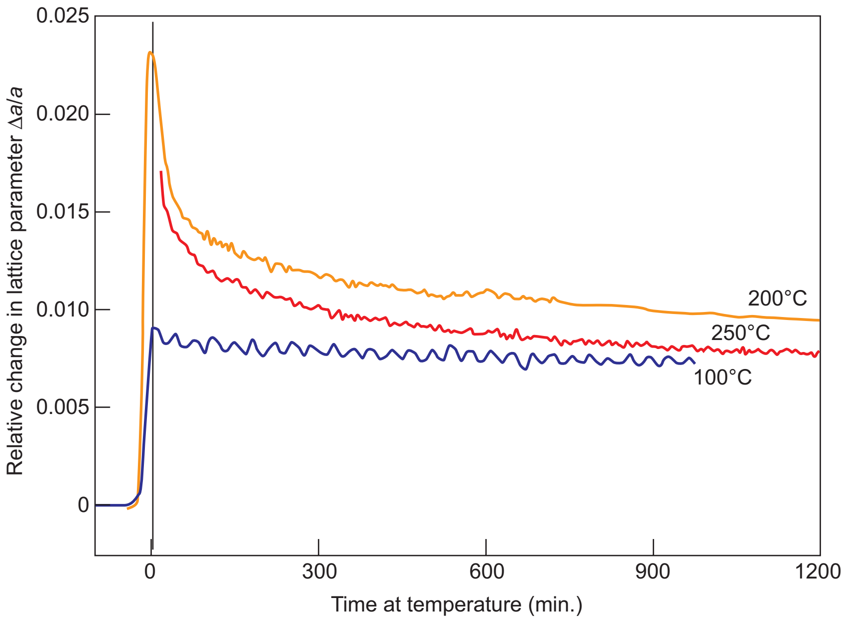

Figure 5. Changes in the U-6Nb's Lattice Parameter vs Dwell Time at Three Temperatures
Relative changes in the U-6Nb lattice parameter are plotted for 100ºC, 200ºC, and 250ºC. These changes are attributed to the niobium leaving the solid solution of the majority α″-phase.

occurs in hours or days (comparable to the time available in a typical neutron-diffraction measurement). In a typical aging experiment, a sample is heated to between 100°C and 300°C and held at constant temperature for approximately 24 hours while neutron diffraction data are collected at 5-minute intervals. During this time, changes in the lattice parameters (obtained from the diffraction data) occur and can be expressed as strains relative to the lattice parameter at the start of the test. Figure 5 illustrates the strain changes of the U-6Nb lattice parameter for three temperatures. The changes in the lattice parameter can be attributed to niobium leaving the solution, and by combining the results from Figures 4 and 5, it is possible to estimate the niobium left in solution. For instance, after 2 hours at 200°C, the niobium content was reduced from 5.75 wt% to roughly 5.25 wt%; after 17 hours, it was further reduced to 4.8 wt%. Since the measurements cannot determine where the niobium goes, the neutron measurements are complemented by other techniques such as transmission electron microscopy.

Different Deformation Mechanisms for 6 wt% and 7 wt% Niobium

The stress–strain responses shown in Figure 2 indicate the complicated nature of the plastic deformation of U-6Nb. Indeed, early versions of the mechanical threshold strength (MTS) model (Chen and Gray 1996), which is widely used to model dynamic materials properties, did not effectively describe the double-yield behavior. The first plateau in U-6Nb is known to be caused by twinning. However, comparable mechanisms for other uranium-niobium compositions are not well understood. For this reason, in situ neutron-diffraction measurements were performed under load for

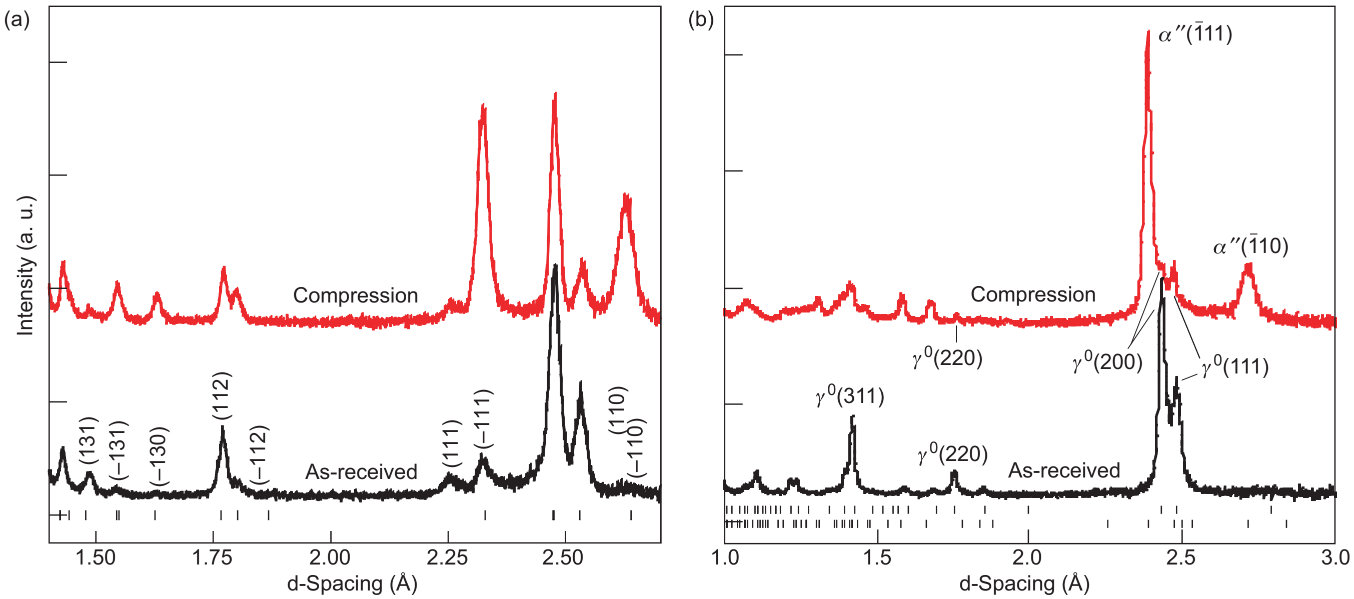

Figure 6. Neutron Diffraction Patterns for U-6Nb and U-7Nb

Plot (a) is for U-6Nb and (b) is for U-7Nb. Both plots show neutron-diffraction patterns for as-received material and after 4% plastic deformation (compression). (a) Changes in peak intensity and the absence of new peaks are an indication of twinning. (b) The presence of new peaks observed in this case is an indication of a phase transformation from γ^0 to α''.

different niobium compositions. These measurements indicated a significant metallurgical difference between the deformation mechanisms seen in U-6Nb (α'' monoclinic phase) and in U-7Nb (γ^0 tetragonal phase). Figure 6 shows diffraction patterns in the as-received condition and after 4 percent compressive strain for both materials. Figure 6a shows the data for U-6Nb. Changes in peak intensity, indicating rapid texture change, are clear, but no new peaks appear. This behavior is a signature of twinning. However, in Figure 6b, which shows the data for U-7Nb, comparison of the diffraction patterns for the as-received condition and after 4 percent compressive strain show the presence of new peaks, which is symptomatic of a stress-induced phase transformation from γ^0 to the α''. The understanding obtained from these experiments has led to improving the MTS model by incorporating twinning. This improvement resulted in more faithful modeling of the double-yield stress-strain response of U-6Nb.

Future Measurements

Our current work has established the baseline properties of U-6Nb. The neutron diffraction measurements at LANSCE have added insight to the deformation mechanisms and to the niobium redistribution kinetics. The next steps are to look at the deformation properties of aged material and to quantify the activation energy for aging by analyzing data from a variety of tests. Finally, we wish to link aging-related property degradation to performance. ■

Acknowledgments

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Further Reading

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