Electron microscopy of some exotic materials

T. E. Mitchell

Center for Materials Science
Los Alamos National Laboratory
Los Alamos, NM 87545, USA

Just about every material has been looked at under the microscope, either out of pure inquisitiveness or the need to relate the microstructure to its properties. Some of these materials are mundane, like steels or glass or polyethylene; others are so-called advanced, such as intermetallics, silicon nitride or zirconia; yet others might be called exotic whether they be martian rocks, high temperature superconductors, fullerenes, diamonds, or the latest thin film device. Many exotic materials are important in Los Alamos, not only weapons materials such as actinides, tritium and explosives, but also civilian materials for energy applications. Here we will report briefly on plutonium and uranium, on rhenium disilicide, and on Cu-Nb nanolayered composites.

Plutonium has an astonishing six allotropes. Preparation of thin films for TEM is probably more difficult than any other material, not only because of its radioactivity but also because of its toxicity and rapid reaction with oxygen. (A thin foil will burn in air!) Pu is usually alloyed with Ga to stabilize the δ (fcc) structure. A typical microstructure is shown in figure 1. Note the helium gas bubbles at the grain boundaries, formed from α radioactivity; these are potentially embrittling. If less Ga is added, the β (monoclinic) structure is stabilized [1]. In this case twinning is common, as shown in figure 2.

Uranium has a variety of uses (not only nuclear) because of its high density. It has “only” 3 allotropes and is often alloyed with Nb to improve its corrosion resistance and ductility. Nb helps stabilize the high temperature bcc γ phase but the Nb wants to come out of solution during cooling. Rapid cooling leads to the formation of a twinned martensite structure, as shown in figure 3. This so-called α” structure is supersaturated with Nb and can be heat-treated to optimize properties [2].

Rhenium disilicide is one of the few compounds reported to have the tetragonal C11b, MoSi2, structure. However, it apparently is Si-deficient and probably has a Re₆Si₇ stoichiometry [3]. This would give it an even number of electrons per atom and explain why it is a semi-conductor (with potential applications as an infrared detector). TEM has revealed that Re₆Si₇ has an astonishing array of incommensurate structures and distortions. There is an incommensurate modulation along the a-axis with a periodicity of 1.2 nm (= 3.8a), as shown in figure 4. The two sets of extra spots in the diffraction pattern are due to the fact that two twin variants are included. The splitting of the 220 spot is due to a ~0.6% orthorhombic distortion. There is a second incommensuration along the c-axis with a periodicity ~8-9nm. In addition, careful study of HOLZ reflections in [100] diffraction patterns reveals splitting corresponding to a monoclinic distortion with β~89.9° accompanied by twinning on (001). Other transformed structures are observed. All of this suggests that the Re₆Si₇ is in a state of frustration with the underlying C11b structure, probably due to the difficulty of accommodating Si vacancies.

There is a great deal of interest in artificial nanolayered materials because of the possibility of creating materials with unique tailor-made properties. An example is nanolayered Cu/Nb. Wires of Cu/Nb can be drawn with high strength and high electrical conductivity with potential application for high field magnets. Even higher strengths can be achieved with nanolayered Cu/Nb because an even smaller length scale can be achieved [4]. Furthermore, for thicknesses ~1 nm or less, the Cu is in the unusual bcc form, as shown in figure 5. Apparently the Cu templates on top of the bcc Nb during deposition, in spite of the more than 10% difference in atomic size. For thicker films of Cu the strain build-up is such that the bcc Cu transforms martensitically to the normal fcc form (figure 6).

References


FIG. 1 - Helium bubbles in fcc δ-Plutonium (courtesy of T. G. Zocco).

FIG. 2 - Twins in monoclinic β-Plutonium (courtesy of T. G. Zocco).

FIG. 3 - Twins in monoclinic α″-Uranium (courtesy of P. G. Kotula).

FIG. 4 - Incommensurate structure with two twin variants in Re₄Si₇.

FIG. 5 - 11Å Cu/Nb multilayer showing bcc Cu.

FIG. 6 - 50Å Cu/Nb multilayer. The boxed region shows the sharp transition from fcc Cu to bcc Nb.