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New Applications and Novel Processing of Refractory Metal Alloys

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Summary:

Refractory metals have often been limited in their application because of their propensity to oxidize and to undergo a loss of yield strength at elevated temperatures. However, recent developments in both processing and alloy composition have opened the possibility that these materials might be used in structural applications that were not considered possible in the past. At the same time, the use of refractory metals in the electronics industry is growing, particularly with the use of tantalum as a diffusion barrier for copper metallization. Finally, the application of grain boundary engineering to the problem of intergranular fracture in these materials may allow processes to be developed that will produce alloys with a greater resistance to fracture.

Keywords:

chemical-mechanical polishing, Cr-Ta composites, CVD deposition, EBSD, electronics applications, grain boundary engineering, melt processing, Nb-silicide composites, sputtering

1. Introduction:

The refractory metals are usually defined to be molybdenum, tungsten, niobium, and tantalum. They have a body-centered-cubic structure and have among the highest melting points of all of the elements. They also have high densities; the lightest, niobium, has a density of 8.58 g/cc that is comparable to nickel (8.55 g/cc), but tungsten, the heaviest, has a density of 19.2 gr/cc. Other properties are summarized in Table I.

The most attractive feature of these elements is their high melting points, but this positive attribute is offset by other less favorable properties, such as their rapid oxidation rate at temperatures well below the melting temperature and loss of strength at high temperatures (1). Consequently, in the past these

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metals and their alloys have primarily been used either at room temperature where oxidation and strength loss is not a problem or in inert environments at high temperatures where they are protected from environmental interactions and high strength is not required. Processing has also proved difficult. Most of these materials are prepared by powder metallurgy instead of melting techniques, and this fact has limited extensive alloy development. Furthermore, molybdenum and tungsten tend to be very brittle at room temperature, and any thermomechanical processing of these materials must be performed at elevated temperatures (1,2).
In recent years, there have been several new thrusts in which the use of these materials is critical. In the area of structural materials, alloys have been developed that have good high temperature strength and oxidation resistance, thus allowing them to be considered for use in aircraft engine and land based turbines (3-6). At the same time, refractories are used extensively in the electronics industry in a variety of applications (1,7). Tungsten has been used for a number of years as the vias in integrated circuits, and tantalum films are now used as a diffusion barrier in the preparation of integrated circuits by copper metallization. At the same time several new techniques have been developed that can allow a more detailed examination of the microstructure of refractory metals. Chief among these is electron energy backscattering diffraction (EBSD) (8). This technique can be used to determine the texture of materials and to understand how this texture evolves during processing.

Table I
Properties of Refractory Metals

Element	Nb	Ta	Mo	W
Structure	BCC	BCC	BCC	BCC
Melting Point (°C)	2468	2996	2617	3410
Elastic Modulus (GPa)	110.3	186.2	289.6	358.5
Density (g/cc)	8.58	16.7	10.3	19.3
Thermal Conductivity (cal/cm/°C/s)	0.125	0.130	0.34	0.397

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All of these developments are closely tied with new processes for preparing these materials. Thus to review new refractory-based alloys, we will organize this paper by the different ways in which the processing can take place. To begin, we will consider solidification of refractory-based alloys and, in particular, the use of directional solidification in preparing these materials. The next brief section will consider powder processing. The third section will examine thermomechanical processing and show the power of EBSD to help design new processes that can produce materials with better properties. Finally, we will discuss various thin film/electronic applications of refractory metals.

2. Melt Processing of Refractory Metals:

Because of the high melting point of refractory-based materials and their reactivity with the environment at high temperature, standard casting procedures are usually not applicable for these alloys. However, in recent years directional solidification methods have been used to make refractory metal intermetallic composites that have the potential to replace nickel-base superalloys in the hottest sections of aircraft engine turbines (3). These composites, which are the subject of paper 10-RM5 in this session, are composed of a Nb-based solid solution, which provides room temperature toughness, and niobium silicides, such as Nb_3Si and Nb_5Si_3, which provide high temperature strength. Other alloying elements can be included in these materials to provide oxidation resistance or to change the type of silicide present. These composites have been prepared by a variety of methods including physical vapor deposition (PVD) (9), foil laminates processing (10), and arc-casting(4). However, one of the most promising techniques is directional solidification, since it allows great control over the distribution of the phases in the material and can also be used to prepare large ingots of the material.

One way in which directional solidification can be achieved is through the optical image float zone method used by Pope (11). The basic principle of this method is very similar to zone refining in that a small molten zone is translated along the rod. As it passes along the rod, it deposits material in such a way that a directionally solidified material is formed. The heating is performed with tungsten halogen lamps in a water-cooled chamber as shown in Figure 1. Although this technique has not been used to prepare Nb-silicide composites, Pope has prepared directionally solidified ingots of a number of intermetallic compounds and has performed extensive research on the

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composite system Cr_2Nb/Nb (11). A typical microstructure of this system is shown in Figure 2.

Bewlay *et al.* (3,12) have demonstrated that the Czochralski technique can also be used to make directionally solidified structures. The alloy is melted through induction levitation in a segmented, water-cooled crucible. A seed is lowered into the liquid and slowly withdrawn, producing the ingot. This method has been applied to the preparation of niobium-silicide composites with melting temperatures up to ~2300°C. Figure 3 shows an example of a microstructure prepared by this method.

The properties of these Nb-silicide composites indicate that with proper optimization of the alloy composition, both good creep properties and good oxidation resistance can be maintained. Figure 4 shows the creep rate of Nb-Si alloys tested in compression at 1200°C under constant load (13). These materials contained alloying additions of Ti and Hf, both of which improve oxidation resistance of the Nb-silicide base materials. The results show that the addition of up to 25 at.% Ti and 8 at.% Hf do not adversely affect the creep rate. However, if concentrations above these values are used, the creep rate increases to levels of 10^{-5} s^{-1}, which would be unacceptable for aircraft turbine applications.

Figure 5 shows the oxidation resistance of the niobium-silicide materials (3,4,14). One can observe that through appropriate use of alloying elements, the oxidation rate can be greatly reduced with respect to more traditional monolithic Nb-based alloys. It has been found that Hf and Ti should be increased substantially to provide good oxidation resistance and that addition of Al is also very beneficial. Creep studies clearly show that if these elements are increased beyond certain limits the creep rate is too high for the alloy to be useful (13). However, the potential of these alloys, which would allow an approximately 200°C increase in the operating temperature of the turbine (3), mandates that research continue to find optimal alloying combinations.

Land-based turbines do not require the high temperatures of aircraft engine turbines, and other materials can thus be considered. Significant progress has been made in recent years in developing Cr-based alloys for these applications. Although Cr is not usually considered as a refractory metal, the material being developed at Oak Ridge National Labs and described in detail in paper 108RM5, uses Ta as the principal alloying element (5,6).

The Cr-Ta system has a eutectic at ~ 10 atomic percent Ta. The two phases that form at the eutectic are a Cr-rich solid solution and a Cr_2Ta Laves phase. With appropriate processing the Laves phase may either be dispersed in the solid solution or in a lamellar eutectic structure. In addition other elements

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such as Mo, Ti, Si and La have been added to provide solid solution strengthening and/or oxidation resistance.
Figure 6 shows the creep behavior of these materials (5,6). This figure demonstrates clearly the role that microstructure plays in determining the creep resistance of these materials. The sample with the dispersed Laves phase showed a much higher creep rate than the material with the cast lamellar structure. This result on the creep behavior of Cr-Ta alloys underscores the importance of alloy architecture in determining creep strength. It would appear that lamellar structures could well be optimal because of the lay-out of the ductile phase with respect to the strengthening phase. If the strengthening phase has too low a volume fraction or is in very coarse particles, one can have a continuous pathway of the ductile phase that can creep readily and provide a continuous ductile pathway throughout the material.
We have chosen to focus on the two alloy classes listed above, because they have the potential to bring new refractory-based alloys into production. However, melting techniques are also being applied to more traditional alloys as well. Tantalum is another refractory metal that is usually prepared by vacuum melting techniques. These have recently been reviewed by Moser (15) and can be divided into two main processes: vacuum arc remelting and electron beam drip melting. Electron beam melting is usually the first step in the process and because of the high temperatures involved it also leads to purification of the metal. All interstitials will be evaporated during this step; the primary remaining impurities will be other refractory metals. The ingots made by electron beam methods are often further refined by vacuum arc remelting. This technique provides better mixing and can further refine the material. Multiple melting and solidification are often performed before the ingot is ready for further processing.

3. Powder Processing of Refractory-Based Alloys:

Powder processing of refractory metals is the more standard method of preparing large scale pieces of these materials. In general, the material is pressed into shape and then sintered by passing an electrical current through the pre-form (16). This sintering process provides sufficient strength to allow the material to be processed by standard thermomechanical methods.
Some of the most thorough studies of the pressing and sintering processes have been performed on non-sag tungsten that is used in the incandescent lighting industry for lamp filaments (16,17). In this case, the sintering also sets the composition of the material so that it contains the required amount of

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potassium to obtain the non-sag behavior. Today, much of the alloy development that is being performed on refractory metals uses powder-based methods. Some of the most recent interesting advances in this area have been reviewed by Capus (18).

4. Thermomechanical Processing of Refractory-Based Alloys:

The standard methods of thermomechanical processing of refractory metals have always been rolling, forging, swaging, and wire drawing. The specific requirements can vary from one metal to another. For example, Ta can be worked at room temperature because of its great ductility. In contrast, Mo and especially W must be processed at elevated temperatures to avoid cracking. Information about various processing methods have been given in other publications (19-23).

Although details of these processes are undoubtedly important, we wish to examine in this section a new technique that allows thermomechanical processing to be followed much more closely and that should aid in the solution of various processing problems. This technique is referred to as EBSD and when coupled with various orientation imaging methods allows the details of microstructural evolution during processing to be followed.

The basic technology has been reviewed in numerous publications and will only briefly be considered here (8). Basically, one places the sample in the scanning electron microscope and allows the beam to fall on the sample at a glancing angle. Kikuchi bands are generated that can be analyzed for crystallographic information. Since the beam can be focused to a very small diameter, the crystallographic information can be obtained from a single grain. If the beam is then rastered across the surface, an orientation map, such as the one shown in Figure 7, can be produced.

Several studies of this type have been reported for refractory metals. Briant *et al.* (23) have followed the evolution of texture in annealed tantalum. In that study, only crystallographic information was obtained, which was plotted in the form of inverse pole figures as shown in Figure 8. These results show that the normal direction to the plate evolved into a <111> texture with continued deformation and recrystallization. In contrast the deformation in the rolling direction after recrystallization did not have a strong character. More recently, Briant and Jepson (24) have used this technique to study texture evolution in tantalum samples processed for sputtering. Such a technique allows one to observed texture banding in processed samples. For example, a comparison of Figures 9a and b show that there is a strong <111> texture component in the area shown in Figure 9b that is not present in

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Figure 9a, even though both maps were taken from the same sample. Thus by understanding these changes in texture one can design processes to control its evolution.
Another important outgrowth of this process has been the development of the field of grain boundary engineering. It is well known that tungsten and molybdenum are very prone to intergranular fracture. This fracture always occurs along high angle grain boundaries; special grain boundaries (i.e. those with low Σ values) and low angle grain boundaries are much less prone to fracture (25). If one could increase the number of special boundaries relative to random high angle grain boundaries, one could inhibit intergranular fracture. The use of EBSD makes determination of this grain boundary structure straightforward.
Watanabe and Tsurekawa (26) have performed studies this type for molybdenum polycrystals. They processed samples by two different routes. One consisted of swaging the material to a diameter of 10 mm at elevated temperatures. Sheets were then cut from the rod and annealed in vacuum at 1773 or 1873K. The second set of samples was prepared from a single crystal of Mo that was forged to induce deformation. Sheets were then removed and annealed as described above. The latter method produced a much higher number of special boundaries than the first method. When these samples were tested in four point bending, it was found that the latter samples showed an approximately 100 MPa increase in fracture stress. The fracture mode for the samples containing the higher number of special boundaries was predominantly transgranular whereas the samples processed by the other method failed intergranularly. The authors further showed that in order to achieve this improvement in fracture strength approximately 20% of the boundaries must have this special character.

5. Deposition of Refractory Metals from a Vapor Source:

Today there are a number of uses of refractory metals in the electronics industry and their criticality to this industry has led to significant research in a number of areas. One of the main uses of refractory metals in this field is the tungsten vias in integrated circuits. These are the parts of the circuit that connect the layers of wiring to one another. The process of making vias begins with the patterning of the cylindrical holes in the silica that make the appropriate connections between the layers. It is then necessary to fill these holes with an electrical conductor. The primary reason why tungsten was chosen for this application was its ability to be deposited by a chemical vapor

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deposition (CVD) process. In this process tungsten, in the form of WF_6, is passed over the substrate and the following reaction occurs.

$$WF_6 + 3H_2 \rightarrow W + 6HF$$

If the proper conditions are set up, the vias will be uniformly filled and appropriate connections made (27).

Once the CVD operation is complete, it is necessary to remove all the tungsten that has deposited on the surface that is not contained in the vias. Some efforts have been made to develop selective deposition, but the most common approach is to use chemical-mechanical polishing to remove the excess tungsten. Obviously, for such a process the details of material removal must be controlled very accurately, and research has shown that both the pressure on the sample and the pH of the solution are important variables in this process (28-30). The mechanism for this process is thought to be a combination of chemical and mechanical effects. When the tungsten is polished in a slurry, an oxide will rapidly form. Any protrusions will be knocked off by abrasive particles and bare surface exposed. As the oxide reforms, corrosion occurs and reduces the roughness of the surface. This process continues until the required surface planarity is achieved.

One of the major new applications for tantalum in the electronics industry is its use as a diffusion barrier between electrodeposited copper and silicon. In the past, aluminum has been used for most wiring in integrated circuits because it was difficult to process the copper and keep it from diffusing into the silicon. However, copper is preferred because of its higher electrical conductivity. The application of a tantalum diffusion barrier, which is produced by sputtering, can stop the diffusion of copper into the silicon (31, 32). Therefore the broad application of copper metallization in integrated circuits may also lead to new developments in the manufacturing of tantalum sputtering targets.

6. Summary:

This paper has reviewed a number of new materials and new processing applications for refractory metals. The new alloys being developed for various structural applications indicate that new markets may soon become available for these materials. At the same time applications in the electronics area continue to grow. New techniques are becoming available that allow the microstructure evolution during processing to be followed closely.

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7. Acknowlegments:

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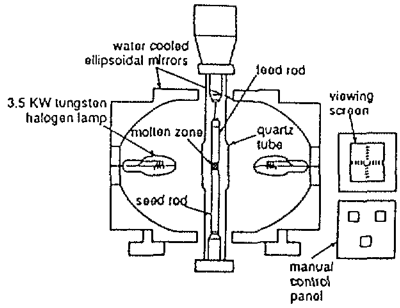

Figure 1 – A schematic of the optical imaging float zone furnace used for directional solidification of refractory based materials. Figure taken from reference 11.

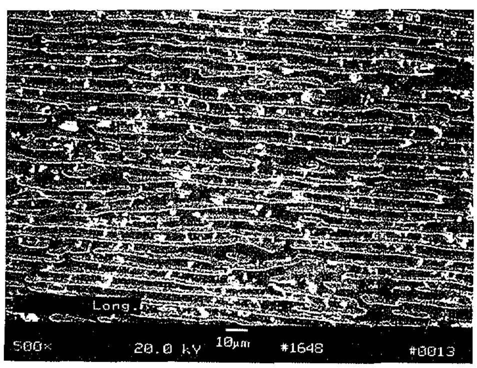

Figure 2 – Microstructures prepared by the optical imaging float zone furnace. The microstructure is from a 44Nb-54Cr alloy. The lighter phase is the Nb solid solution. The micrograph is taken parallel to the growth direction of the composite. Figure taken from Reference 11.

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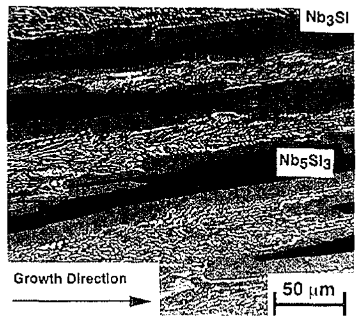

Figure 3: The microstructure of a niobium silicide in-situ composite prepared by directional solidification. Micrograph courtesy of B.P. Bewlay of the General Electric Company.

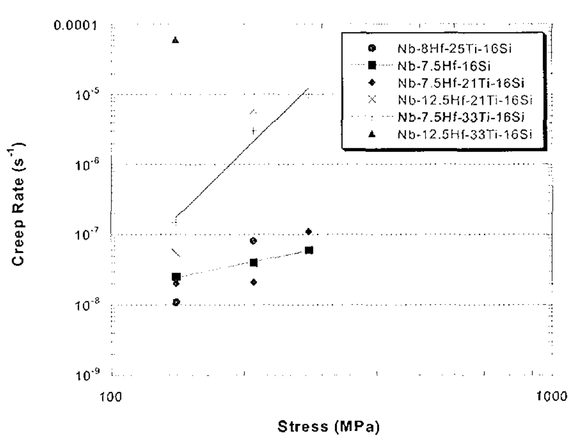

Figure 4 – Creep rates of five Nb-silicide based in situ composites. The samples were tested in compression at 1200°C. Note that additions of Ti and Hf above 25 and 8%, respectively, causes the creep rate to increase significantly. Data taken from reference 13.

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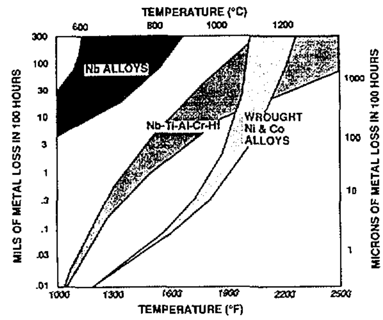

Figure 5 – A comparison of the oxidation of Nb-based material with the oxidation of Ni- and Co-based superalloys. Note that the addition of Ti, Hf, and Al greatly reduces the oxidation rate over that for monolithic Nb alloys that do not contain these additions. Figure courtesy of Dr. M.R. Jackson of the General Electric Research and Development Center.

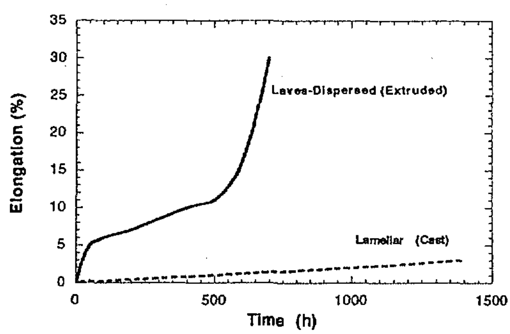

Figure 6 – Creep results for Cr-Ta alloys. Note that the as-case material with a lamellar structure showed very little elongation during the test run at 1000°C and 138 MPa in humid air. The composition of the alloy was Cr-8Ta-5Mo-0.5Ti-0.01Ce. Figure courtesy of Dr. Michael Brady of Oak Ridge National Labs.

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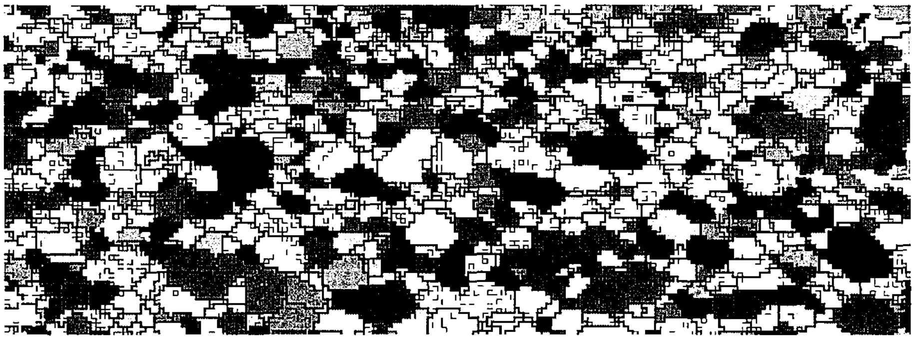

Figure 7 – An orientation map of a sample of tantalum. The grains colored red all had <110> directions within 20° of the direction parallel to the long dimension of the figure.

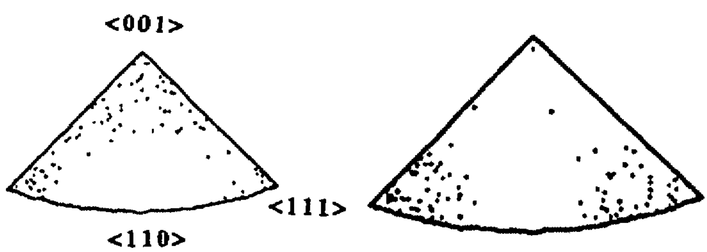

Figure 8 – Inverse pole figures for rolled and recrystallized tantalum. (a.) The inverse pole figure for a sample rolled to 2.8 mm and recrystallized. (b.) The inverse pole figure for a sample rolled to 0.13 mm and recrystallized. In both cases the direction of the inverse pole figure was that perpendicular to the rolling surface. Note that with continued deformation and recrystallization, the texture becomes strongly <110>.

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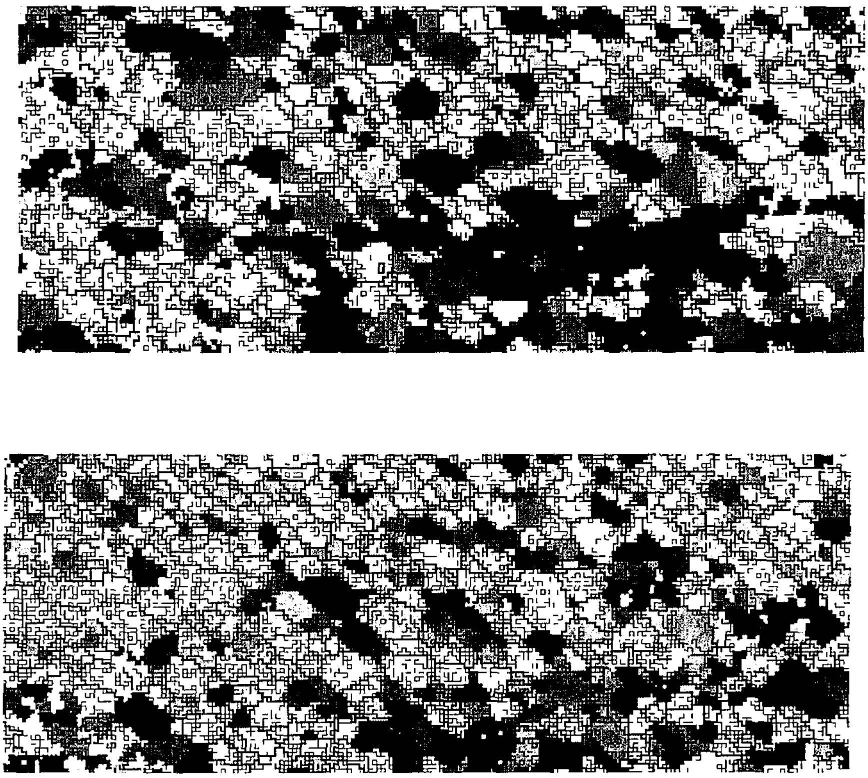

Figure 9 – A comparison of orientation maps showing banding in the texture. In these figures, which were taken from different regions of the same sample, the grains colored blue have <001> orientations with 20° of the long dimension of the figure and those colored yellow have <111> orientations within 20° of this dimension. Note that in the upper figure <001> predominates and in the lower both the <111> and <001> are present.