3.5. PREPARATION OF SPECIMENS FOR ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY

Table 3.5.1.1. *Chemical etchants used for preparing thin foils from single-crystal ceramic materials; symbols: I immersion method; SFJ separatory funnel jet; CJ convection jet; BJ boiling jet*

Material	Etchant		References
Al_2O_3	85% H_3PO_4, 723–733 K	*I*, BJ	Tighe (1964)
$BaTiO_3$	H_2SO_4	CJ	Kirkpatrick & Amelinckx (1962)
$CaCO_3$	$C_6H_8O_7$ (dilute)	*I*	Braillon *et al.* (1974)
CoO	85% H_3PO_4	CJ	Remaut *et al.* (1964)
$LiNbO_3$	KOH, 623–673 K	*I*	Wicks & Lewis (1968)
MgO	85% H_3PO_4, 373 K	*I*, SFJ	Washburn *et al.* (1960)
$MgAl_2O_4$	85% H_3PO_4, 523–723 K	*I*	Lewis (1966)
MnO	$HCl + NO_3$		Barber & Evans (1970)
SiO_2	$NH_4F \cdot HF$, 453–473 K	*I*	Tighe (unpublished)
	HF, 373 K	*I*	
TiO_2	NaOH, 823 K	*I*	Barber & Farabaugh (1965)
$ZrSiO_4$	$NH_4F \cdot HF + KF$ (1:1), 693–703 K	*I*	Tighe (unpublished)
$Y_3Al_5O_{12}$	85% H_3PO_4, 573 K	*I*	Keast (1967)

respect to grain boundaries, dislocations, and other types of interfaces found in the thin foils. The severity of the orange-peel texture increases with bombardment time.

Subsurface ion damage occurs and is imaged as spotty black-dot contrast that is typical of point-defect clusters. The presence of the ion damage affects experiments that involve heating of the thin foil but is otherwise accepted as an artefact of the process. In materials such as silicon, the ion damage is sufficient to cause vitrification of the specimen at or near the surface. The argon that is implanted in specimens can be detected with the element-analysis systems.

One troublesome artefact of the ion-thinning process is the surface contamination that is produced by sputtering from tantalum or molybdenum or stainless steel parts of the specimen holder and the cathode. Debris may interfere with the analysis. The sputter debris is frequently located along interfaces of cracks and pores and adds to the contrast effects. Additional contamination occurs during one-sided thinning. The sputter debris adheres to the non-thinning side and must be removed by light-ion etching at the end of the thinning process.

3.5.1.4. *Final thinning by chemical etching*

Chemical dissolution methods for preparing electron-transparent specimens were developed before ion thinning was perfected. These methods are not used extensively, but they have some advantages particularly where ion thinning may disturb the surface composition or structure of a particular material. It is advantageous to use chemical dissolution in some stages of specimen preparation, for example to relate etch pits to dislocations, to prepare a defect-free surface, and to remove the ion-damaged surface from thin disc specimens (Barber & Tighe, 1965). The thinning conditions must be chosen carefully to avoid artefacts such as preferential dissolution at grain boundaries, precipitates, and dislocations, or surface precipitates produced by a supersaturated solution.

Suitable solvents and dissolution conditions must be found for each new material. Some of the chemical etchants used for thin-section preparation are listed in Table 3.5.1.1.

Devices that squirt a jet of chemical solvent at the disc or slab specimen are used to obtain careful control over the final thinning to electron transparency (Kirkpatrick & Amelinckx, 1962; Tighe, 1964; Washburn, Groves, Kelly & Williamson, 1960).

Predictable dissolution rates are obtained by varying the concentration and temperature of the etchant. Solutions can be found that will produce a smooth surface polish or an etch-pitted surface. For example, corundum is etched in boiling phosphoric acid at a temperature approximately 50 K lower than the temperature used for polishing. Surfaces with different crystallographic orientations have different dissolution rates. Useful sources of information about possible etchants are mineralogical and chemical handbooks that discuss production of etch figures and crystallographic facets (Dana & Ford, 1922; Honess, 1927).

3.5.1.5. *Evaporated and sputtered thin films*

Thin nonmetallic films are prepared by electron-beam heating and by plasma sputtering for direct applications such as optical and dielectric films and for standard samples for calibration of the X-ray and electron-energy-loss element-analysis spectrometers on the electron microscopes. The thickness, crystallinity, and composition of the evaporated films are determined by the method of deposition. Co-evaporation from several electron-beam sources is used to produce films of different composition. Reproducible polycrystalline as well as amorphous microstructures are produced using heated and unheated substrates of glass, mica, metal, carbon. The crystalline electron-beam-evaporated films are used for diffraction standards and have been used to observe line broadening and lattice-spacing shifts that result from strain and compositional differences in the films.

Glasses with known compositions are used as sources for plasma sputtering to make thin-film composition standards. Such standards are required for quantitative analysis of ceramic transmission-electron-microscope specimens.

3.5.2. Metals

The aim of the specimen preparation is to obtain a sample (thin foil) of adequate electron transparency to permit the acquisition of images and diffraction patterns of the internal microstructure that is unaltered by the preparation method from that existing in the bulk material. When transmission electron microscopy is carried out at 100 to 200 keV, the sample thickness must lie in the range 0–1000 nm. The useable thickness decreases with increasing mean atomic number and with the requirement for ultra-high (atomic) resolution or for *in situ* chemical analysis by electron-energy-loss spectroscopy (Penneycook, 1981, 1982). In metallic systems, which can undergo plastic (permanent)

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