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Thin Foils of Non-Metals Made for Electron Microscopy by Sputter-Etching*

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Established techniques of making thin foils of non-metallic materials are reviewed briefly and their inadequacies outlined. The preparation of foils by sputter-etching is described and the effects on the sample of ion current density, and angle of ion incidence are discussed. Results on specimens of ceramics, glasses and minerals are presented. From these it is concluded that sputter-etching is a valuable and near-universal thinning technique for non-metals.

1. Introduction

There are numerous problems concerning the microstructure of polycrystalline non-metallic materials which could benefit from the application of transmission electron microscopy (TEM). They include the topographical features of phase transformations, the distribution of microporosity, segregation of second phases, chemical reactions in the solid state, domain studies, etc. But relatively little progress has been made because of the difficulties encountered in making suitable specimens. For normal TEM at 100 kV, thin sections or foils of thickness ~ 0.2 μm are necessary. Foils which are an order of magnitude thicker will probably prove to be quite acceptable for high voltage instruments. In both cases, the preparation technique should give foils which are uniform in thickness over areas ~ 10 μm^2 or more, unbuckled, strain-free and devoid of surface structure. To be realistic, no technique is likely to achieve all of these aims for non-metals. However, most of the existing methods fall very far short of the ideal and lack of better technology is the main block to progress.

Studies on non-metals by TEM have been largely confined to those with layer structures and crystals whose natural growth habit includes platelets or whiskers. Numerous references to such studies have been given by Amelinckx [1] and by Hirsch *et al* [2]. Results have also been obtained from single crystal foils thinned by chemical dissolution; the materials studied include magnesium oxide [3], magnesium fluoride [4], aluminium oxide [5], titanium dioxide [6] and beryllium oxide [7]. However, chemical thinning is seldom of use with polycrystalline and multiphase materials because of the occurrence of preferential attack at internal surfaces and leaching of second phases. Nevertheless, Stewart and Green [8] and James and McMillan [9] have thinned certain glasses with apparent success.

A simple and common method of preparing non-metals for TEM is by crushing; there are also slightly less crude fracture techniques. Although they are unreproducible, wasteful and incapable of yielding data from pre-selected regions, they have given valuable results. Prebus and Michener [10] were first to use crushing for glasses; the technique has also been used on minerals such as feldspars [11, 12], quartz [13] and zircon [14].

In addition to the methods already mentioned, there exists one technique of preparing foils which is demonstrably fairly wide in application. This is thinning by mechanical polishing, as developed by Doherty and Leombruno [15] for use on glass-ceramics, and subsequently modified by others. The technique has been used with considerable success in a few laboratories and it can yield foils ~ 0.1 μm thick. It consists of glueing

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one flat polished face of a sample slice to a plastic support, and then grinding and polishing the other surface until a foil of suitable thickness is formed. The mechanism of transfer of the foil to a supporting grid is critical and with multicomponent systems, care is necessary if the leaching-out of some phases is to be avoided. The study of certain glasses with the Doherty and Leombruno method and with fracture methods has been discussed by Seward *et al* [16].

The main disadvantages of Doherty and Leombruno's method are that it is time-consuming and requires skilled technical operators. Moreover, it does not work well with porous materials owing to filling in of the voids. However, at this time it is the only established method of a nearly universal nature. The rest of this paper will attempt to show that another technique, based on sputter-etching with energetic positive ions, also yields highly satisfactory foils of glasses, minerals and ceramics.

2. The Preparation of Thin Foils by Sputter-Etching

2.1. Previous Work

Cathodic sputtering is the process by which atoms or molecules are ejected from a target subjected to bombardment with positive ions. The sputtering effect has been known for over a century [17] and is now commonly used in the production of high purity thin films. The term cathodic sputtering embraces two situations: (i) the target is made the cathode in a simple gas discharge vessel; (ii) the target is quite separate from the source of positive ions and its electrical and gaseous environment is therefore subject to more control. For the purpose of this paper it is important to distinguish these two cases. It is also important to avoid confusion between the preparation of thin films by the condensation of sputtered atoms and the preparation of thin foils by removing atoms by sputtering. To this end, the latter preparation process will be referred to as sputter-etching or ion-erosion. The underlying physical processes by which atoms of a target are evaporated as a result of interactions with ions in the incident beam are still not clear. But it is established that the atoms ejected from the target receive their energy from internal target atoms, displaced as a result of a chain of interactions initiated by an incident ion. The sputtering mechanism and possible modifications to the subsurface structure are not unimportant if TEM is to be performed on samples thinned by sputter-etching.

The use of energetic ions to process crystal surfaces is not particularly new. There are several instances of the use of ion-bombardment to create surface relief and reveal microstructures. To quote some examples, Keig and Haines [18] used ion-bombardment to expose the structures of plutonium ceramics while Krokhina *et al* [19] have studied glass-ceramics. Further observations of surface structure have arisen from the many experiments on ion-channelling in the last few years.

A great deal of work on ion-bombardment was carried out in the 1950's by Castaing, Trillat and others. Much of this work was not published. The first reported successful use of sputter-etching to produce thin foils for TEM appears to be that of Heitel and Meyerhoff [20]. They placed a silicon sample in a ring-shaped cathode and used a 1.5 kV argon discharge in a magnetic field (Penning-type arrangement) to erode the two principal surfaces of the sample. In this way they were able to make single crystal foils $\sim$ 100 Å thick. Sputtering from two crystal faces simultaneously was also used by Genty [21] and by Paulus and Reverchon [22]. The former employed 4 keV argon ions to erode the surfaces of metals at normal incidence. Paulus, however, introduced several significant refinements into his apparatus. One of these allowed the sample to be rotated slowly in two opposing ion beams at a predetermined shallow angle, hence eroding two surfaces uniformly and simultaneously. The variation of sputtering rate with ion energy and angle of incidence was investigated. In the energy range 3 to 12 keV, the sputtering rate was a maximum for an angle of 15°; this was demonstrated for several crystallographic orientations. Paulus and Reverchon showed that their apparatus could produce thin foils of materials which were porous and of high-resistivity, in particular, ferrites. Tighe [23] in the U S A is currently using a commercial copy of Paulus's apparatus to study a variety of ceramic materials.

Drum [24], Shimomura *et al* [25] and, more recently, Hirthe *et al* [26] have prepared thin foils by placing material on the cathode plates in conventional DC discharge sputtering systems. Drum worked on Al_2O_3 and SiC, Shimomura on NiO and Hirthe on TiO_2. In all cases the incident ion beams were inclined at 90° to the crystal surface. Only Hirthe claims to have prepared foils free from signs of ion damage.

2.2. Design of Sputter-Etching Apparatus

When preparing thin foils it is important to keep their temperature sufficiently low to avoid structural changes. Consequently, ion current densities in excess of ~ 200 μA/cm^2 are unnecessary. This is a factor of 10^{-1} to 10^{-2} lower than the ion density in normal sputtering systems. Moreover, if the ion energy is increased beyond ~ 10 keV, most of the increase is dissipated in deeper penetration (which is clearly undesirable) and not in greater efficiency of sputtering [27]. These modest requirements for sputter-etching show that one can use inexpensive cold cathode ion sources which work by extracting ions from a glow discharge.

The author's system essentially comprises an evacuated bombardment chamber into which protrude the two ion sources and the shaft carrying the sample holder (fig. 1). The ion guns are of the hollow anode type and each produces seven separate parallel ion beams. Each anode is connected through a large ballast resistor to a well-stabilised 10 kV, 10 mA DC supply. The bombardment chamber is mounted over a 6 in. diffusion pump and liquid nitrogen trap, backed by a two-stage rotary pump. This vacuum system produces a pumping rate at the chamber of 300 l sec^{-1}. This is necessary to maintain a working vacuum of between 10^{-3} and 10^{-4} torr while high purity argon gas is entering the anode-cathode interspace through fine needle valves. The main disadvantage of the cold cathode ion source is that it necessitates a relatively large flow of gas into the system. With a typical gas flow rate of $\sim 5 \times 10^{-2}$ torr l sec^{-1} there is an ion current of about 70 μA per gun at 6 kV. The ion current density at the sample is about 200 μA cm^{-2}. The ion currents can be measured and balanced by means of retractable probes. Fig. 2 (a) is a photograph of the exterior of the sputter-etching chamber, while fig. 2b is a close-up of the interior through the front window.

The sample, with its periphery sandwiched in a thin stainless steel holder, is rotated in the ion beams at 6 rpm. The inclination of its exposed surfaces with respect to the beams can be preset at angles between 0 and 30°. It is important that the ion beams should "see" both surfaces and erode them at equal rates if no provision is made to stop the back-diffusion of sputtered atoms from the sample and its holder. To minimise the redeposition of sputtered material on the sample, there is a partial shield around it (visible in fig. 2b) which is cooled by liquid nitrogen. The shield also prevents the occurrence of arc discharges in the ion guns when thinning materials which give off volatile constituents. Eventually the ion sources become electrically unstable to glow discharge because of enlargement of the holes in the cathodes. In normal use, however, they have a life of about 150 h.

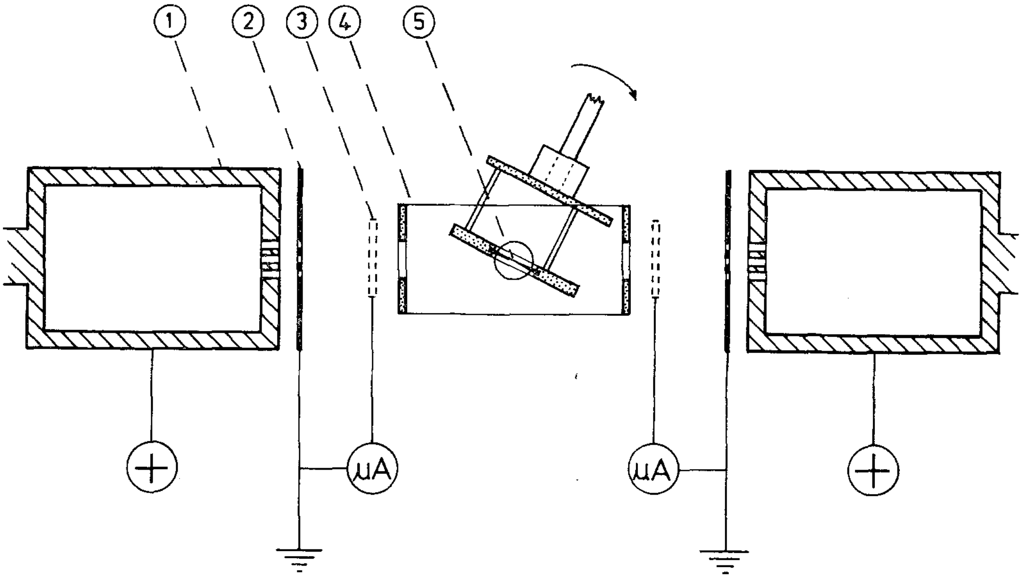

Figure 1 Schematic diagram of ion bombardment assembly: 1 – pierced hollow anode, 2 – pierced planar cathode, 3 – electrode for monitoring ion current, 4 – liquid nitrogen cooled shield, 5 – preshaped sample.

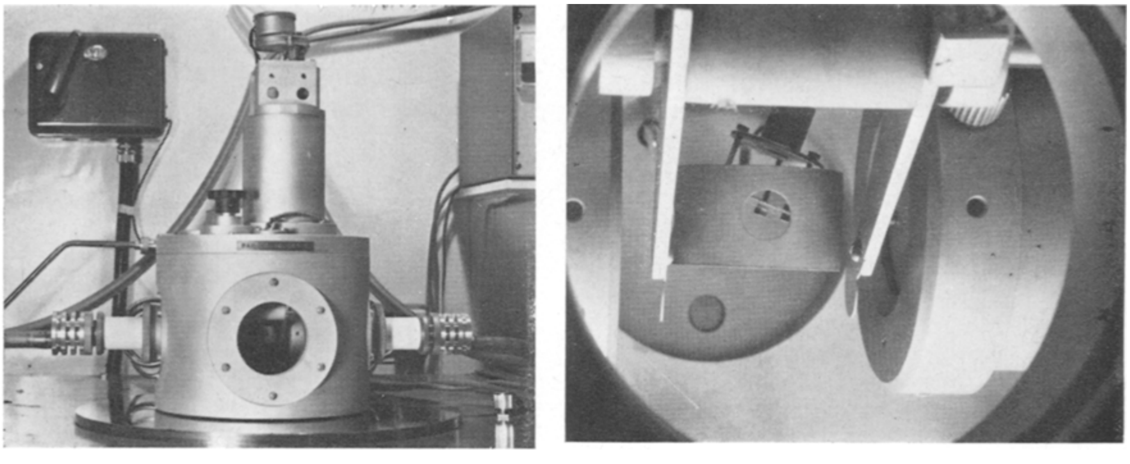

Figure 2 (a) View of exterior of bombardment chamber. (b) Interior of bombardment chamber, showing disposition of specimen holder, cooled shield and ion source.

2.3. Preparation of Samples

Typical erosion rates for ceramics such as dense alumina are found to be about 1 to 2 μm per hour per surface for a glancing angle of 20° and an ion current density of 200 μA cm^{-2}. This can be converted into a sputtering ratio, giving a value of about 1 molecule per ion. Where possible, it is desirable to start with samples not more than 25 to 30 μm thick. With porous or friable materials thicker samples may have to be used. For convenience in electron microscopy, thinning is usually carried out on disc-shaped samples, 3 mm in diameter. These are normally preshaped to give a central thin area ~ 30 μm thick, while the rim thickness is ~ 250 μm. If petrographic thin sections are available they can be thinned with ease and yield very good foils, since the surfaces suffer uniform erosion and remain substantially parallel. To give added strength to petrographic sections they are cemented before thinning to an electron microscope grid with its central area cut out.

3. Some Observations on Foils made by Sputter-Etching

The major part of the author's work has been on glass samples and minerals. But to illustrate the capabilities of the ion-erosion method, it is of value to consider first conventional ceramic materials, these being more commonly recognised and understood. Fig. 3 is an electron micrograph of a sample of high purity dense alumina with an average grain size of ~ 2 μm. As the micrograph suggests, there are large areas in the foil which are fairly uniform in thickness. Angular pores occur at many grain-boundary junctions but there is no porosity and little dislocation structure within grains. The ion-bombardment has produced some surface irregularity but this is not very apparent in the electron microscope unless a region is in a strongly-diffracting orientation. These observations may be compared with the results of Tighe and Hyman [28] on foils of other types of alumina. Fig. 4 indicates what can be achieved with a multiphase dense ceramic, namely, an aluminous porcelain for electrical applications. The rounded grains are embedded in a glassy matrix which is, of course, less transparent to electrons than the crystalline material. The

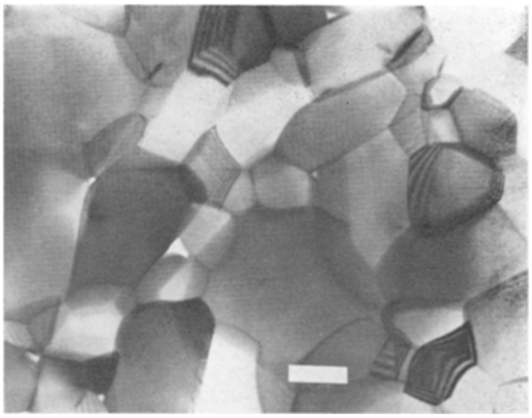

Figure 3 Transmission electron micrograph of fine-grain high purity alumina. Bar mark = 1 μm.

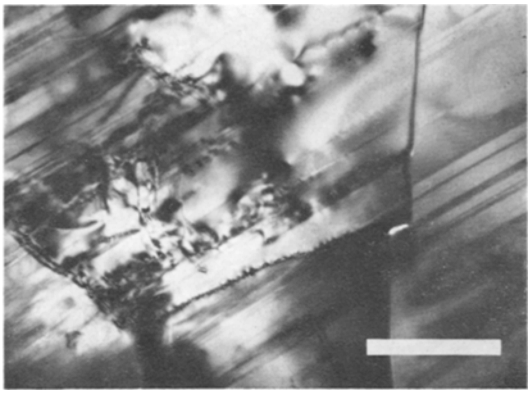

Figure 4 Transmission electron micrograph of foil taken from a porcelain high voltage insulator. Bar mark = 1 μm.

greater electron absorption and scattering power of glasses requires that glass and glass-ceramic foils ideally should be ~ 1000 to 1500 Å thick for ease of study. Foils which are suitably thin and free from significant surface relief can be prepared if the areas presented by the different phases are reasonably small (~ 5 μm diameter) and they are uniformly distributed. This has been established with several types of crystallised glass. It is demonstrated for the case of a heat-treated glass in the $Na_2O - MgO - Al_2O_3 - SiO_2$ system, with some fluorine substituted for oxygen, in fig. 5. Within the temperature range 850 to 950° C for this glass, crystal growth occurs as spherulites of small platelets, mainly of wollastonite. In glasses where larger crystallites have grown, ~ 10 μm long, difficulty has been found in making good foils and troublesome local variations in thickness can occur. This is shown in fig. 6, an electron micrograph of a large dendritic crystal of diopside in glass.

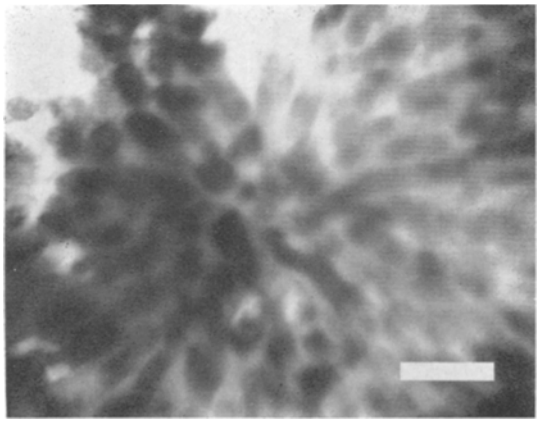

Figure 5 Transmission electron micrograph of spherulitic structure in a glass of the soda-lime-alumina-silica system, with some fluorine substitution of oxygen. The main crystalline phase is wollastonite. Bar mark = 1 μm.

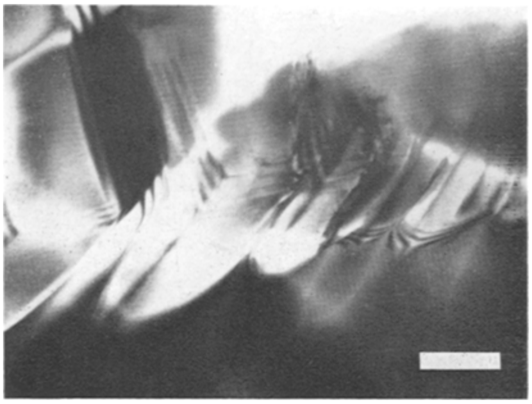

Figure 6 Transmission electron micrograph of part of a large diopside dendrite in a glassy matrix. Bar mark = 1 μm.

A direct comparison between TEM observations of foils made by sputter-etching and of fragments produced by ultramicrotomy [29] has been possible with a commercial glass-ceramic (Corning 9608). As a control experiment on ion-thinned foils the results are reassuring; no differences are seen in the appearance and distribution of phases, nor are the different surface conditions apparent. Of course, the sputter-etched foils do afford greater ease of handling and provide larger continuous thin areas for study. Fig. 7 shows type 9608 glass after crystallisation heat-treatment; the major crystalline phase is β-eucryptite, the lathe-like crystals are thought to be rutile.

Mineralogical specimens from which the author has made foils include olivine rocks, obsidian glass and several varieties of silica: agate, banded chalcedony, rutilated quartz, amethyst and "Tiger Eye" (fibrous quartz with asbestos and other mineral inclusions). Several of the foils were made directly from petrographic sections, as described earlier. All the minerals yielded excellent foils without apparent loss of inclusions or changes in structure. The results show that the ion-erosion technique can be of considerable value to mineralogists. With the aid of foils made by the author, Champness [30]

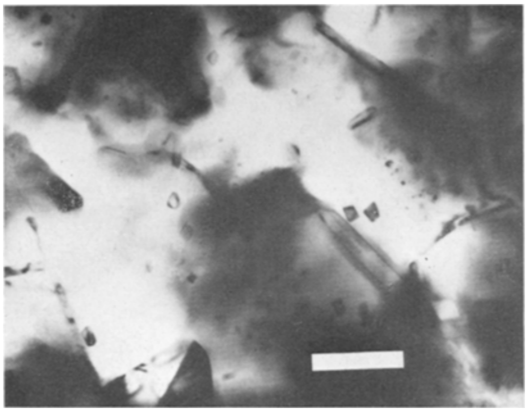

Figure 7 Transmission electron micrograph of Corning 9608 glass, fully crystallised. Bar mark = 0·5 μm.

has been studying the oxidation of hortonolite, a mineral belonging to the olivine group, containing about 47% Fe_2SiO_4. It was necessary to make one foil containing an external surface. This was achieved by operating one ion source only, apart from a brief period of two-beam sputter-etching to render both foil surfaces clean. A similar problem has been met recently in making foils from oxide layers on corroded ferrous components.

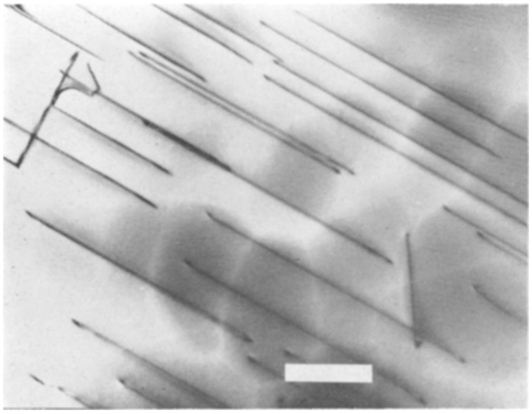

Figure 8 Transmission electron micrograph of dislocations in hortonolite, an olivine mineral. Bar mark=1 μm.

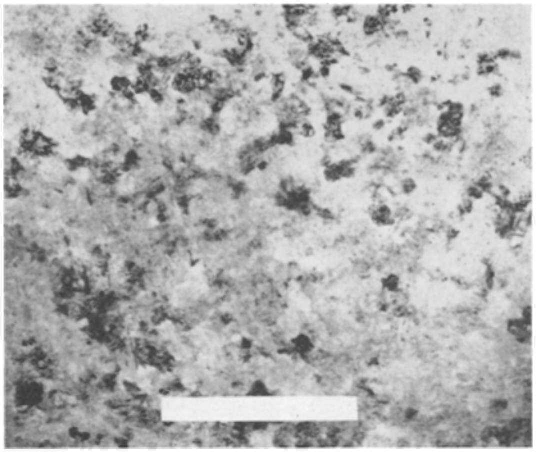

Figure 9 Transmission electron micrograph of agate. Bar mark = 0·5 μm.

To illustrate the value of the ion-thinning method to minerals, fig. 8 shows an array of dislocations in a hortonolite grain, with little sign of surface structure due to sputtering. The microcrystalline fibrous structure of agate is shown in fig. 9; because of the fine scale of the crystallinity, the foil has extensive regions of uniform thickness. Results of the work on agate and chalcedony will be reported elsewhere.

4. Discussion

It has already been mentioned that the sputtering rate increases with increasing angle between the ion trajectories and the surface normal. Paulus and Reverchon [22] and Almèn and Brucé [27] have shown that the sputtering ratio S_ϕ at an angle ϕ is equal to S_0 sec $^{3/2}\phi$, where S_0 is the ratio at normal incidence. Stewart and Thompson [31] have argued theoretically that bombardment at a glancing angle of 15 to 20° will give the optimum erosion rate. In practice, the geometry of many samples makes it difficult to achieve angles less than 20°. But shallow angles of beam incidence are certainly desirable if the differential etching of grains and phases is to be avoided. The creation of some types of surface relief is enhanced at glancing angles; this includes the production of furrows and hillocks in the shadow zone of precipitates and other crystal defects. Mazey *et al* [32] have shown that ion-channelling and internal structural defects can also give rise to surface structure in crystals[*] but sputter-etched glasses can exhibit similar features [33]. Rotation of the sample during ion-bombardment minimises the creation of surface structure which might otherwise result from subsurface structural defects.

It is clearly important that the sample temperature does not rise sufficiently during bom-

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[*] With low ion energies, the sputtering rate is highest on close-packed crystal planes so that internal defects develop as hillocks when they approach the surface. A hillock will form around a subsurface defect because it will create a shadow region in the surface for outwardly displaced target atoms.

bardment to cause structural modifications. Other workers [26] have made qualitative estimates of specimen temperatures during cathodic etching. Measurements have been made on the author's bombardment unit, using a fine copper-constantan thermocouple embedded in a glass sample blank of near-standard dimensions, gripped in the usual sample holder. On starting the ion guns the temperature of the sample rose for 15 min, finally reaching a value of 127° C. This figure is unlikely to differ by more than ~ 20° C from one ceramic/glass specimen to another. It is certainly low enough to remove fears of physical or chemical changes occurring at a significant rate.

A more basic problem with some materials is the occurrence of ion-induced radiation damage. Calculation shows that with 6 keV argon ions the depth of penetration in most refractory oxides is ~ 300 Å. A layer of this thickness can be removed chemically from thin foils of certain polycrystalline materials (e.g. Al_2O_3) without their being seriously broken up by preferential etching along grain-boundaries, etc. But where such a chemical treatment is undesirable, any ion damage which occurs cannot be removed without annealing and causing further structural changes. In practice, the occurrence of ion damage is seldom troublesome and it is less obvious in complex materials than in single crystals. The images of the defect clusters formed are small, ~ 100 Å in diameter. Normally they are easily distinguished from innate structural features within crystalline phases. Defect clusters are not, of course, seen in glassy phases because they do not exhibit diffraction contrast. In glass-ceramics damage is seldom seen in small crystalline inclusions, partly because of the low probability of their being correctly oriented to show strong diffraction contrast, and often because they have remained encased within the foil during ion-bombardment.

Glasses scatter electrons diffusely and the images seen by TEM lack contrast; for this reason alone, it is desirable that foils should not be more than ~ 1000 Å thick. Moreover, electrons are strongly absorbed and with thicker foils it is easy to induce changes through excessive heating in the electron beam. Surface melting can easily occur and this has been reported by several workers. In a thick absorbing sputter-etched glass foil another effect is also observed; this is the creation of minute voids and bubbles. It seems likely that this is due to the aggregation of atomic argon implanted in the foil during thinning.

The mechanism by which argon ions are neutralised at the sample surface is not yet established. It is apparent from the observed sputtering ratio and from the absence of a dark space near the sample that insulator samples do not acquire significant positive charges. The explanation is thought to be that the ion beams impinge not only on the sample but also on its stainless steel holder. In this way a large number of secondary electrons are created and fed into the plasma surrounding the sample; a rough calculation suggests that there would be sufficient to effect neutralisation.

5. Conclusions

Although sputter-etching has not been widely used as a means of making thin foils of non-metals, the foregoing results suggest that it has a great potential. There are still many aspects of ion-etching to be investigated in respect of erosion rates, the creation of surface structure etc, and in the wider context of the interaction of ions with solids and the formation of radiation damage. But as yet, it seems that there are no important differences between foils made by ion-erosion and those prepared by more established methods.

Even with the technique there will still be ceramics to which TEM cannot be applied. Low density insulating bricks of high porosity (those composed mainly of bubble alumina, for example) are probably in this class. But Tighe and Kreglo [34] have made a successful TEM study of sputter-etched foils of a sea water magnesia brick with 19% porosity. Thus the technique supplies the means of studying sub-microstructures in multiphase systems which are otherwise inaccessible. Moreover, there exist interesting possibilities for the ion-bombardment method in the field of solid state research. All of the work described in this article has been concerned with bombardment with argon ions. But if a noble gas is not used, there is a possibility of solid state reactions. On a larger scale, such processes are already being explored – for example, the impurity doping of semiconductors by ion implantation. On the scale necessary for TEM, it has proved possible to produce oriented thin films of ferric oxide, Fe_3O_4 by the bombardment of iron sulphide FeS_2 with oxygen ions [35]. Many other possibilities remain as yet unexplored.

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