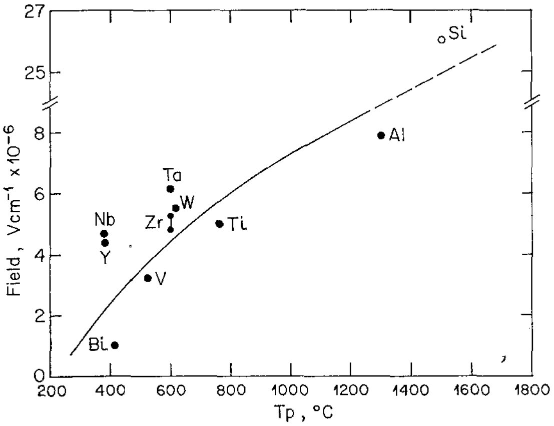

Figure 1 A plot of T_P, in °C, for the thermal oxidation of the shown metals versus the field required to sustain a typical ionic current density (1×10^{-3} A cm^{-2} in the present case) during anodic oxide growth. The T_P values are defined in the text and are from [1]; the values of the anodic field are taken from a previous paper [5].

the *field* needed to sustain a given value of the ionic current density, the latter being responsible for the conversion of the metal to the corresponding oxide in accordance with the well-known Faraday's laws of electrolysis. For the metals for which the data are available in the literature, the driving force needed for the thermal oxidation (T_P) and that for the anodic oxidation (field at a given current density) appear to be roughly correlated (Fig. 1). It is clear that higher T_P values herald higher fields, notwithstanding the broken scale in Fig. 1, which was necessary to accommodate Si. Very high T_P values tend to be associated with very high fields as for the case of Al and Si; conversely, low fields tend to be associated with low T_P values as in the case of Bi. The purpose of this correlation (Fig. 1) is only to show that roughly similar trends are followed by metals with regard to thermal and anodic oxidation. This is, of course, not entirely unexpected since in Equations 1 to 3 the same reaction is always carried out, namely, conversion of M to MO_x, although the means of negotiating the activation energy barriers involved in these reactions are different in the two cases, namely, temperature in the thermal oxidation and applied field in the anodic oxidation.

It should be mentioned that reliable data on the fields required during anodic oxide growth on metals other than those in Fig. 1 are not reliable. In fact, it is not possible to sustain appreciable *anodic* oxide growth on many other metals simply because anodization in electrolyte solutions can lead to other parallel reactions, occurring preferentially to oxide growth; e.g., oxidation of the electrolyte components, oxygen evolution and anodic dissolution of the metal, etc [3, 4].

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A metallic replica technique for scanning electron microscopy

The scanning electron microscope (SEM) is a very useful tool for observing the surface topography of materials. For most metals, it is unnecessary to give the sample any treatment before observation. For non-conductive materials, such as polymers, the usual method to prepare the surface for observation in the SEM is to deposit a thin metal layer on the sample surface. This treatment is usually found to be satisfactory for low magnification (×100 to 1000). For higher magnification, where higher time-average electron beam densities are required, the sample will distort, degrade and often crack in the region of scanning. In an electron beam, polymers do not merely distort owing to differential expansion of different crystalline regions but also undergo irreversible structural changes. For crystalline polymers, such as polyethylene, the electron beam can influence the degree of crystallinity and can produce irradiation damage [1-3]. In polyoxymethylene, the cracks formed in the vapour-deposited metal film scanned by the electron beam were found to be in a certain characteristic pattern revealing the irreversible expansion of the underlying polymer [4]. Such phenomena put a limitation on the usage of SEM on polymers for viewing at high magnification.

The technique reported below surmounts this difficulty by using a thick, indestructible, negative or positive metal replica of the actual surface. A negative metal replica of the polymer surface is made by vapour-depositing a continuous metal film (gold-palladium) of a thickness of about 1000 Å on the sample in vacuum. Then the deposited metal film on the sample is built up in thickness by electroplating with nickel to a thickness of about 0.1 mm, which is found adequate in strength and stiffness for easy handling. The metal replica is then peeled off and is ready for observation. To make a positive metal replica, a plastic negative replica is first made by using commercial replication tape. Then the metal is deposited on the plastic replica in the above manner. To obtain high quality blemish-free replicas, care is taken at the beginning of nickel plating, when the initial vapour-deposited film is still very thin and susceptible to cracking due to heating. A way of avoiding this difficulty is to apply silver paint around the area of interest of the sample to reduce the contact resistance at the boundary of the thin layer and the external circuit. At the very beginning, the plating current density is set at 0.01 A cm^{-2} and is gradually increased to its normal value of 0.02 A cm^{-2}.

The advantages of this technique are: (a) the metallic replica is perfectly stable under prolonged electron-beam scanning at high magnifications; (b) the mechanical strength of such replicas is high enough that in most cases they can be peeled off from the sample, and can be cleaned in various solvents without special precaution. In the conventional replica technique for transmission electron microscopy, detaching and cleaning the final replica are always elaborate processes; (c) because the actual interface of contact between the parent surface and the replica can be viewed directly in this technique, more details of the sample surface should be observable, as contrasted with the conventional way of coating the surface with a 200 to 300 Å thick metal layer.

As an example of the usefulness of this technique, Fig. 1 shows the centre part of an extended-chain polyethylene spherulite. The picture is a positive metal replica which was made from an intermediate replica made with commercial acetyl-cellulose tape. The evaporated metal was a gold/palladium alloy (Pd 40%, Au 60%) and was evaporated in a vacuum of 10^{-5} Torr. The nickel plating bath is of the type used by Watts [5, 6], with an initial plating voltage of about 1.5 V to decrease the plating current density across the boundary of the

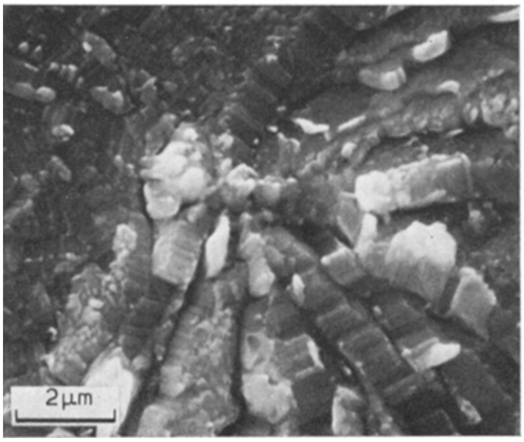

Figure 1 Centre part of an extended chain polyethylene spherulite.

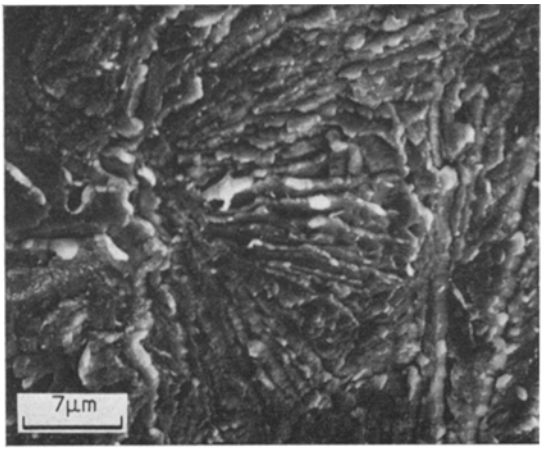

Figure 2 Another area of an extended chain polyethylene showing the artichoke-like structure of a spherulite.

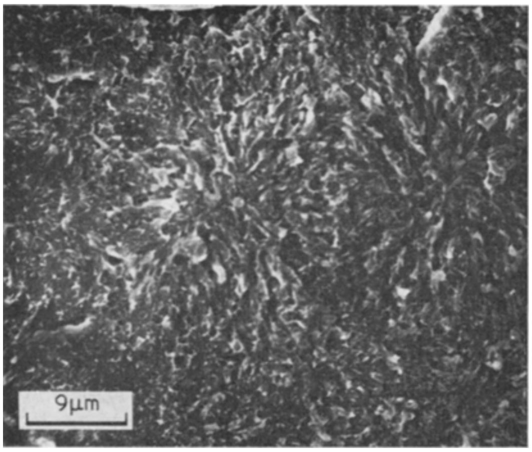

Figure 3 Brittle fracture surface of ordinary high density polyethylene.

initial evaporated coating. After a period of about 15 min, the voltage was increased to 3 V, and maintained at that value until a film thickness of about 0.1 mm is obtained. No residue of the intermediate replica is detectable at this high magnification which normally produces artifacts in the SEM. As expected, the replica is completely unaffected by the electron beam over an indefinitely long period of examination.

The surfaces shown in Figs. 1 and 2 are not conventional brittle fracture surfaces of extended chain polyethylene. These surfaces were produced by first etching a mechanically polished surface with a beam of 4 kV argon ions at 77 K, followed by applying replication tape to the etched surface which strips off a thin layer. The surfaces prepared by this method remain flat on the average and give a more representative view of the underlying spherulite structure than a surface created by brittle fracture. The reason for this is that brittle fracture may start from some weakened sites and may follow some preferential lattice planes or weak interlammellar boundaries. In the stripping technique, a layer of relatively constant thickness, affected by the etching, appears to be removed. It is shown in Fig. 2 that the lamellae in this extended chain polyethylene do not twist at all but, as can be seen in the right half of the picture, the lamellae in a spherulite are arranged similarly to the leaves of an artichoke. Fig. 3 shows a typical fracture surface (produced at 77 K) of a high-density linear polyethylene (Marlex 6009). Two entire spherulites can be seen in this picture. When this picture was viewed together with a corresponding tilted photo as a stereo-pair it could be seen that some lamellae are torn free and stick out of the fracture surface. This suggests that lamellar interfaces are weak planes and can be readily debonded in brittle fracture at low temperature.

We believe that this technique can be applied to all non-conductive materials without any difficulty and without any of the loss of resolution of the surface features that can normally be observed with the SEM. The positive replica technique could also be used as a non-destructive method for metal samples for preserving earlier states of the surface in experiments where surface features change with time.

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