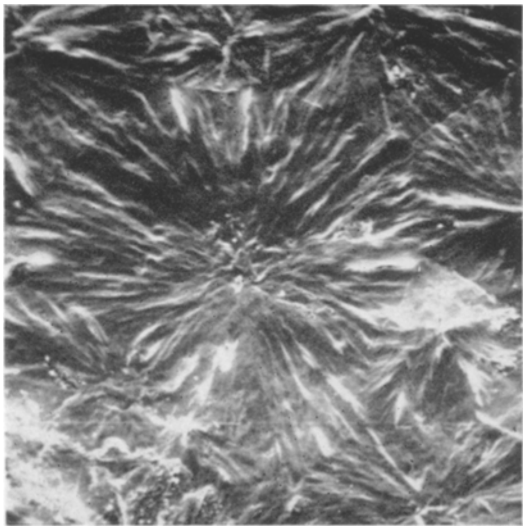

Figure 6 Fully etched polypropylene surface viewed with the Cambridge Instrument Company Stereoscan (×830).

chromic acid. The initial specimens gave spectra agreeing in detail with the results published by Snyder and Schachtschneider [2] and there was no change in the spectra after 500 h treatment with the chromic acid solution.

Discussion

The observations show that 6M chromic acid at 70° C can be used to etch crystalline polypropylene. Treatment times are of the order of 100 h. Chromic acid appears to attack crystalline and amorphous regions at approximately the same rate, thereby removing layers of polypropylene uniformly and revealing the microstructure of the interior. There is no change in density of the bulk specimens after extensive chromic acid treatment, implying that there is no change in percentage crystallinity. The infrared measurements show that there is no obvious change in overall chemical composition.

The chromic acid results are encouraging, for they suggest that it may now be possible to study the microstructures of bulk polypropylene test specimens as they undergo deformation, and hence determine deformation mechanisms. Such a programme of work is under way in the Metallurgy Department at Leeds. Chromic acid etching has also enabled us to determine the mode of fuming nitric acid attack on polypropylene. The results of this work will be published shortly.

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Electrical Conductivity during Hydrogen Reduction of Barium Titanate Single Crystals

In recent years, considerable research effort has been directed to a better understanding of electrical processes in oxygen-deficient barium titanate [1-7] and particularly in single crystals grown by the process described by Remeika [8]. It is well established that single crystals grown by this technique suffer from the incorporation of appreciable concentrations of impurities, notably potassium and fluorine from the solvent.

It has been recently shown by Arend *et al* [7] that these impurities play an important role in the chemical processes which take place during the early stages of the hydrogen reduction of these single crystals. The method employed by Arend involved chemical analysis of crystals reduced in hydrogen at temperatures of 900° C and above for periods from a few minutes to a few hours. This established that there are three regions in which different chemical processes are involved.

Initially, the hydrogen reacts with fluorine present in the crystal to produce hydrogen fluoride. This results in the fast liberation of electrons into the conduction band of the material.

Subsequently, a slower process of volatilisation of titanium fluoride becomes dominant. The release of titanium fluoride is accompanied by a drastic reduction in the number of free electrons in the material.

Finally, when all the fluoride ions in the crystal have been exhausted by these processes, the slow process of formation of water by reduction of the barium titanate forming an oxygen-deficient crystal becomes detectable although the number of electrons liberated by this process remains relatively small at temperatures of 900° C even up to reduction times of 20 h.

Arend gives the reaction equation including all observed processes as

$$
\begin{aligned}
&[Ba_{1-a}K_a]\,Ti[O_{3-a}F_a] + (y+u)H_2 \\
&= xTiF_4 + zTiF_3 + uH_2O + 2yHF \\
&+ [Ba_{1-a}K_a]\,[Ti_{1-x-z}\,(TiV)_{x+z}] \\
&\quad [O_{3-a-u}\,F_{a-4x-2y-3z}\,(AV)_{4x+2y+3z+u}] \\
&+ (2y - z + 2u)\,e
\end{aligned}
$$

where (TiV) and (AV) indicate titanium and anion vacancies respectively.

Concurrent experiments have been performed by the present writers in which flux-grown barium titanate crystals were reduced in hydrogen at 800° C for times up to 15 min. In some of these experiments, platinum paste contacts were applied to opposite faces of the crystal plates allowing two-probe resistance measurements to be made during the reduction process. The result of such an experiment in which the specimen resistance reached a minimum after 5 min reduction is shown in fig. 1. Subsequent reduction up to 20 min resulted in an increased resistance.

Further specimens (obtained from the Harshaw Chemical Co) were reduced without contacts applied, and were allowed to cool to room temperature after varying reduction times. Four-probe resistivity measurements were made on these specimens with current flow in the plane of the crystal plates. Although the crystals are expected to be non-uniformly reduced, since the chemical reactions occur at the surface, a representative average figure for the concentration of electrons should be obtained if the current flow is parallel to the principal faces of the crystal. On this basis, Hall and Seebeck coefficient measurements were made on these plates. The apparatus used was unable to detect a Hall signal indicating a mobility of less than 10^{-5} m^2/Vsec. Seebeck coefficient measurements at 300° K on crystals reduced for more than 5 min were used to determine the electron concentration assuming an electron effective mass of 4.5 m_0 (Berglund and Baer [9]), and a scattering parameter $S = +\frac{1}{2}$. The resulting concentrations were approximately proportional to the conductivity, indicating a mobility near 3×10^{-7} m^2/Vsec. The Seebeck results for crystals reduced for less than 5 min did not lead to similar mobilities, and this may be due to the very high concentration gradients in the crystals during the initial fast reaction.

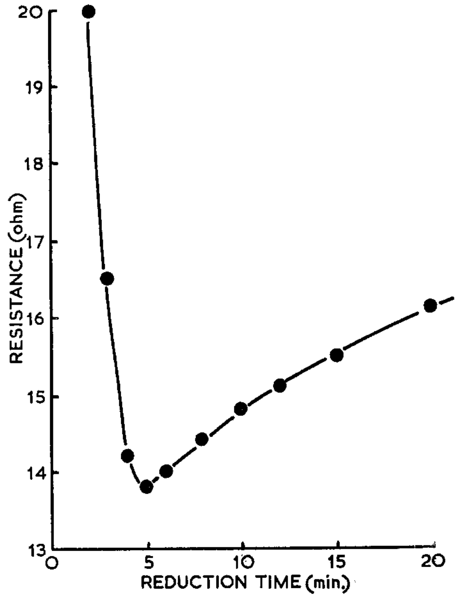

Figure 1 Two-probe resistance of barium titanate flux-grown crystal measured during reduction in hydrogen at 800° C.

The representative electron concentrations calculated from the resistivities using the mobilities obtained at reduction times greater than 5 min are shown in fig. 2 with the results of Arend *et al* for comparison. Agreement between these results is close since the crystals were probably grown under somewhat different conditions and therefore probably contain different initial concentrations of impurities. Furthermore, the shape of the curves depends on the thickness of the crystals. The lower curve of fig, 2 is based on crystals with thickness between 100 and 150 μm.

Further evidence to support the reaction mechanisms proposed by Arend is obtained from measurements made during heat treatments in an inert atmosphere. Of the three reactions proposed by Arend, only the first and last are dependent on

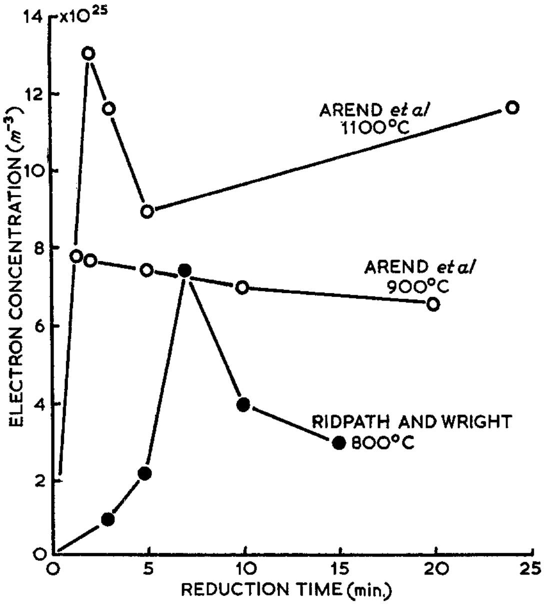

Figure 2 Electron concentration of reduced crystals compared with the results of Arend *et al* [7].

a hydrogen atmosphere. The second, the volatilisation of TiF_3, is expected to take place on heat treatment in the absence of hydrogen. Two-probe resistance measurements have been made in a similar way to that described for the two-probe measurements during reduction, with an ambient of argon at atmospheric pressure. The results are shown in fig. 3, the resistance being expressed as a multiple of the initial resistance. It can be seen that the resistance now increases monotonically as a function of time. This follows from the equation above where y and u are now zero and the change in electron concentration is $-z$.

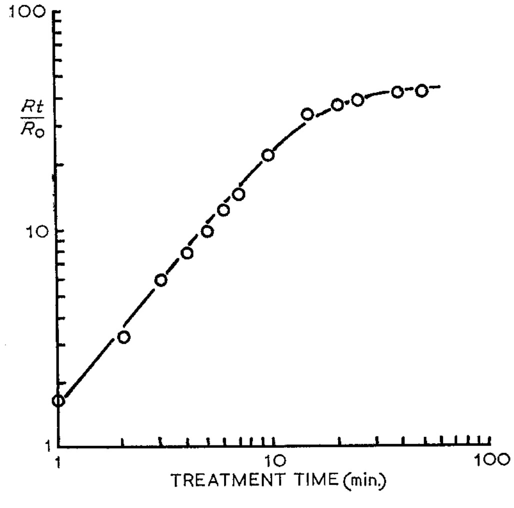

Figure 3 Increase in resistance of flux-grown BaTiO^3 during heat treatment in argon at 800° C.

These electrical resistance measurements correlate directly with the analytical measurements of Arend *et al* and support their proposal that the heat treatment of flux-grown barium titanate in hydrogen results in three reactions, the formation of HF, the volatilisation of TiF_3 and the formation of water.

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