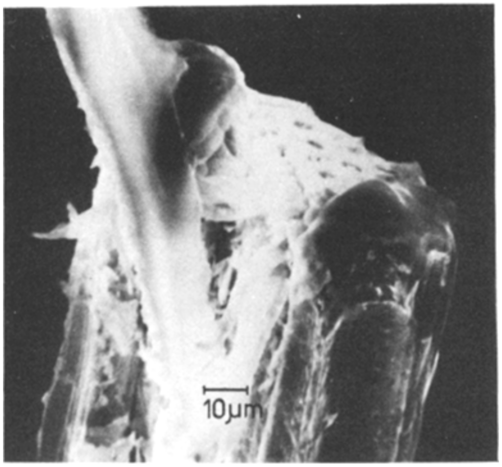

Figure 3 Fractured plant fibre showing cell delamination and cell wall buckling.

closely follows variations in the microstructure of individual fibres. We have observed that each fibre consists of a bundle of about 35 single cells, each cell being about 10 to 20 μm diameter. The cells are held together in the fibre by a mixture of lignin, cellulose and hemicellulose [5]. Page *et al.* [6] have shown that individual cellulose cells may be deformed in tension by as much as 20%, due to the "unconstrained" buckling of the cell walls into the lumen. Similar observations of cell wall buckling have been made by Jeronimidis [1]. This effect has been attributed to the way in which the cellulose microfibrils are wound in the cell walls in a predominantly helical manner [2]. Examination of the fracture surfaces (e.g. Fig. 3) of our notched fibres reveals that the cells undergo lateral separation ahead of the notch (under the action of tensile stresses in the plane of the notch [7]) such that they are then able to deform in the "unconstrained" manner, thus allowing large tensile strains to be achieved in the region of the notch tip. This behaviour is essentially similar to that described by Gordon and Jeronimidis [2] for the failure mechanism of pitchpipe (*Pseudotsuga taxifolia*).

Since the post-buckling deformation is non-elastic it therefore contributes significantly to the energy absorbed as the fracture propagates through the specimen. This energy-absorbing process presumably involves the separation of the helically wound microfibrils and ultimately failure of the microfibrils themselves. Clearly, the adoption of the helical arrangement of reinforcing microfibrils forms the basis of a complex mechanism for the achievement of such high strain energy release rates to obviate the possibility of catastrophic failure within the plant material. Such effects appear to be widespread in nature and would appear to offer great scope for application to synthetic materials.

References

1. G. JERONIMIDIS, *Leiden Botanical Series* 3 (1976) 253.
2. J. E. GORDON and G. JERONIMIDIS, *Nature* 252 (1974) 116.
3. J. F. KNOTT, "Fundamentals of Fracture Mechanics" (Butterworths, London, 1973) p. 105.
4. E. C. McLAUGHLIN and R. A. TAIT, to be published.
5. R. E. MARK, "Cell Wall Mechanics of Tracheids" (Yale University Press, New Haven, 1967) p. 97.
6. D. H. PAGE, F. EL-HOSSEINY and K. WINKLER, *Nature* 229 (1971) 252.
7. J. COOK and J. E. GORDON, *Proc. Roy. Soc.* A282 (1964) 508.

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Effect of magnetic field on reduction of cobalt oxides

In 1972, Skorski [1] noted an increase in the reduction rate of haematite (Fe_2O_3) in a strong magnetic field at 180 and 300° C. Magnetic fields of 500 and 1400 G ($emu\,g^{-1}$) were used. Rowe *et al.* [2] reported on the reduction of the two intermediate iron oxides, magnetite (Fe_3O_4) and wüstite (FeO) to metallic iron at 385 and 490° C, respectively. The reduction of magnetite was shown to be enhanced under the influence of a strong magnetic field whereas that of wüstite was decreased.

Having become convinced that a strong magnetic field can have an appreciable effect on the reduction rate of metal oxides, we now turn our attention to the oxides of cobalt, another ferromagnetic metal. In the present study we reduced both Co_3O_4 and CoO to metallic cobalt. Our technique allows for continuous observation of the reaction parameters during the entire course of the reductions which are carried to completion. The reaction parameters actually measured are sample weight without the magnet and saturation magnetization, an apparent weight, with the magnet. This method represents a significant advantage over the method used by Skorski [1] which involved observation after the fact on reactions not carried to completion.

We used a Cahn thermomagnetic recording balance which has a maximum sensitivity of $\sim 10^{-6}$ g. Samples consisted of ~1 to 14 mg powdered oxides. A thermo-couple placed just beneath the quartz sample pan measured the temperature. The magnetic field was supplied by a permanent magnet of ~4200 Oe. This system was described in greater detail by Rowe *et al.* [2]. The apparatus was flushed with 20% H_2 in N_2 carrier at 65 ml min^{-1} for at least 1 h before each run to assure a constant reaction atmosphere. Runs were made on multiple samples of each oxide, Co_3O_4 and CoO, both with and without the magnetic field.

The rate of reduction of Co_3O_4 and CoO to Co with H_2 at elevated temperatures was measured. The per cent composition was calculated by simple stoichiometry in the experiments run without a magnet. With the magnet in place the situation is distinctly different. Since the Co_3O_4 and CoO are paramagnetic, insertion of the magnet will make the apparent weight of the oxide sample increase slightly. Initially the apparent weight represents 0% metal, 100% oxide. We determined that our CoO, labelled 98% pure, contained ~30% Co initially. However, analysis as described still yields the compositional make-up and does not affect the results or conclusions of this study. Furthermore, the results were confirmed on a second purchase of CoO which was found to be pure. During the course of the reaction, the apparent weight increases strikingly as the paramagnetic cobalt oxides are converted to ferromagnetic Co metal. Points between the initial and final apparent weights are taken to be a linear combination of those weights.

We first analysed the rate of reduction of Co_3O_4 to cobalt using H_2 gas at ~280° C. Five samples ranging from 1.94 to 14.0 mg were run with a strong magnetic field. Four samples ranging from 1.58 to 2.73 mg were analysed in the earth's field. The results are shown in Fig. 1. No systematic variation in reaction rate with sample size was seen within the weight range generally used.

From an examination of Fig. 1 it is seen that an inflection in the curve occurs as the sample changes from Co_3O_4 to CoO when no magnetic field is used. Thus by continuous observation of the mass change we are able to separate the two reductions, $Co_3O_4 \rightarrow CoO$ and the $CoO \rightarrow Co$. This is possible, however, only when the magnet is not in place. The data obtained under the influence of the magnetic field are also shown. In this case, the experimental observation is measurement of the saturation magnetization. Since the saturation magnetization of ferromagnetic cobalt is far greater than that of the paramagnetic Co_3O_4 or CoO, even a small production of cobalt dominates the apparent weight recorded on the balance, and only relatively small change is observed when

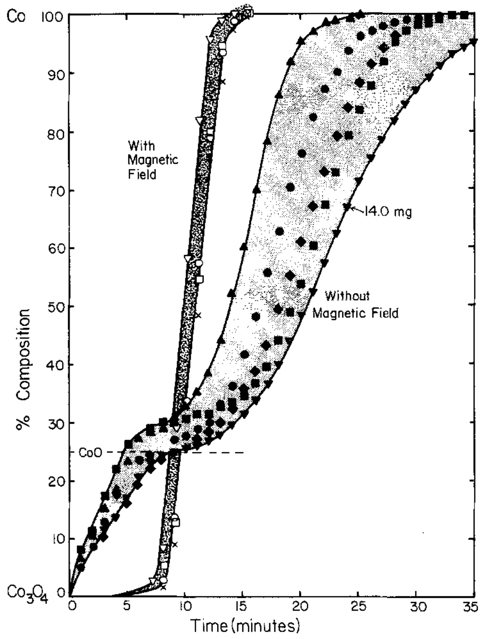

Figure 1 Reduction of Co_3O_4 to metallic Co with 65 ml min^{-1} flow of 20% H_2 in N_2 carrier at ~280° C. Points were hand-read from a strip chart recording for construction of Fig. 1 so that data taken under the influence of a strong magnetic field (changes in saturation magnetization) can be directly compared with those without the strong magnetic field (weight change). Initial Sample weights of Co_3O_4 were: ○, 1.80 mg; ×, 2.39 mg; □, 1.58 mg; ▽, 2.7 mg; ◆, 6.64 mg; ▼ 14.0 mg; ■, 1.94 mg; ●, 6.65 mg; ▲, 3.88 mg.

TABLE I Comparison of the extent of reaction measured by the two different methods utilized in this study, weight versus saturation magnetization

Time	% Co utilizing weight measurement	% Co utilizing saturation magnetization	Difference
14.0 min	24.8	25.0	0.8%
17.0 min	39.3	41.9	6.6%
20.4 min	55.3	56.9	2.9%

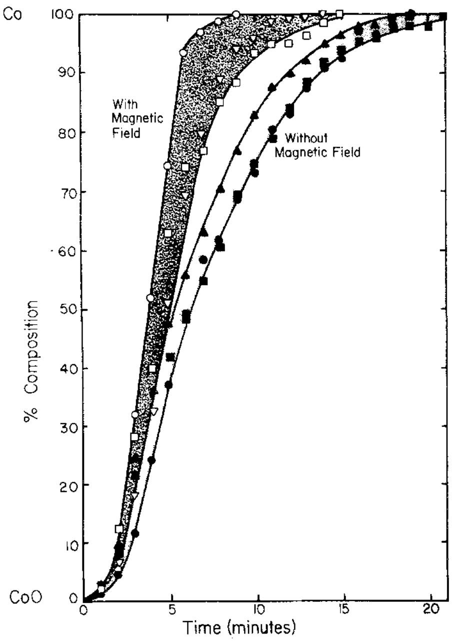

Figure 2 Reduction of CoO to metallic Co with 65 ml min^{-1} flow of 20% in H_2 in N_2 carrier at ~ 200° C. See Fig. 1 caption. Initial sample weights of CoO were: ○, 5.24 mg; ▽, 4.06 mg; ■, 3.72 mg; ▲, 3.95 mg; ■, 5.80 mg; ●, 4.12 mg.

Co_3O_4 converts to CoO. By a comparison of the curves, both with and without the field, we can see that significant production of cobalt clearly begins after about 8 min with the magnetic field which is not noticeably different from the case without the applied magnetic field. From the data in Fig. 1, we conclude that the rate of reduction of CoO to Co is markedly increased by the application of a strong magnetic field. We intend to examine the $Co_3O_4 \rightarrow CoO \rightarrow Co$ with improved technique to hopefully separate more clearly the reduction steps both with and without the magnet.

To confirm our finding that the CoO → Co proceeds more rapidly under a strong magnetic field, we next studied the reduction of CoO to Co directly at ~200° C. The results of this reaction are contained in Fig. 2. Once again we see an increase in the rate of reduction with application of a magnetic field. Note that this is opposite to the effect that Rowe *et al.* [2] found in the analogous reduction of FeO to Fe.

Our results depend on comparison between two types of measurements: weight, with no strong magnetic field, and saturation magnetization, in a strong field. To insure that comparable results are obtained by both techniques, a reduction (similar to those in Fig. 2) was carried out. However, the magnet was moved into and out of the reaction region several times and the actual sample weight was recorded. Calculation of the % composition by both methods allows a direct comparison as shown in Table I. The two different methods of observation of the reaction progress yield % compositions which differ by only 3.4% on average, well within our experimental uncertainty.

While there is now little doubt that a strong magnetic field can have an appreciable effect on reduction rate, the nature of this effect cannot be explained at present. Further study will concentrate on attempts to separate each step of the reduction process by careful oxygen fugacity control.

Acknowledgement

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References

1. R. SKORSKI, *Nature Phys. Sci.* **240** (1972) 15.
2. M. W. ROWE, S. M. LAKE and R. FANICK, *ibid* **226** (1977) 612.

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