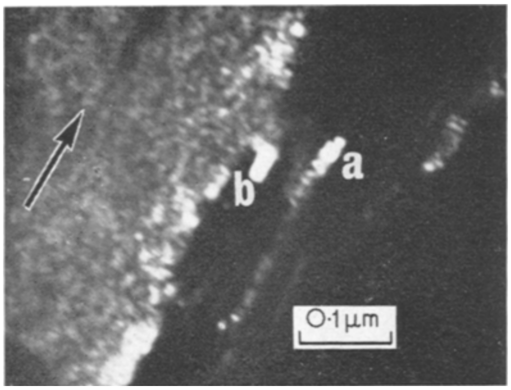

Figure 4 Dark-field electron micrograph using the (002) reflection of the peripheral region around an internal flaw in a fibre graphitised at 2100° C for 10 min.

Mechanical tests on recrystallised fibres show that the fracture strength is reduced in the presence of single crystal graphite platelets [8], possibly due to platelets oriented perpendicular to the fibre axis such that the weak bonding between basal layers is aligned along the stress axis.

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References

1. D. V. BADAMI, J. C. JOINER, and G. A. JONES, *Nature* **215** (1967) 386.
2. D. J. JOHNSON and C. N. TYSON, *Brit. J. Appl. Phys.* **2** (1969) 787.
3. J. A. HUGO, V. A. PHILLIPS, and B. W. ROBERTS, *Nature* **226** (1970) 144.
4. E. R. STOVER, *Metals Progress* **83** (1963) 112.
5. L. M. GILLIN and A. KELLY, *J. Mater. Sci.* **3** (1968) 408.
6. R. BACON and M. M. TANG, *Carbon* **2** (1964) 221.
7. R. PERRET and W. RULAND, *J. Appl. Cryst.* **2** (1969) 209.
8. R. A. COYLE, L. M. GILLIN, and B. J. WICKS, *Nature* **226** (1970) 257.

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B. J. WICKS
Aeronautical Research Laboratories
Melbourne, Australia

A Note on the Stoichiometry Limits in NiO and Fe$_2$O$_3$

The oxygen rich stoichiometry limits in many oxide systems have not in general been well defined. The desirable gas-solid oxidation reaction path has the considerable experimental disadvantage that high oxygen pressures must be contained for long periods of time in pressure vessels operating at relatively high temperatures. Alternative reaction paths, for example the production of oxides in degradation reactions, often lead to uncertainty about the purity, and therefore, the stoichiometry of the oxide sample obtained.

The chemistry of the oxides of the later transition metals suffers particularly from this lack of definition. Here, we report on the oxygen-rich stoichiometry limits in the iron-oxygen and nickel-oxygen systems. In the iron-oxygen system, the oxides up to Fe_2O_3 are well established and preparable by direct oxidation. One higher oxide, FeO_2, has been reported to form in the thermal decomposition of $FeO(NO_3)$ [1], but no characterisation has been given. Contrary to this result, the maximum Fe^{+4} concentration at 500° C and 10 kbar in the ternary system Fe-Cr-O does not exceed 15 % along the tie-line between sesquioxide and dioxide [2].

In the nickel-oxygen system similar discrepancies are to be found. Bogatsky [3-5] has reported that only three compositions (NiO, Ni_2O_3 and NiO_2) of some 25 nickel oxides reported to exist, can be positively identified as separate distinct phases. Ni_2O_3 was identified in the dehydration of nickel nitrate and NiO_2 in the dehydration of nickel oxide hydrate. Kuznetsov [6] has, however, suggested that all these higher oxides and oxide solid solutions are in fact merely partial hydroxide decomposition products. All workers agree that the direct oxidation reaction leads only to nickel monoxide at low gas pressures, but it has been reported [7] that the oxidation can proceed to $NiO_{1.07}$ in oxygen pressures of 300 bar. These data are to be compared with the very limited excess oxygen content reported at higher temperatures [8] and oxygen pressures [9].

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Our experiments have consisted of the equilibration of samples of Johnson Matthey "Specpure" nickel monoxide and iron sesquioxide at 500 and 700° C for periods of one week at 1 kbar oxygen pressure. The high pressure oxidation equipment was as previously described [9] and the materials were analysed for metal concentration, the presence of oxidising valencies and by X-ray diffraction before and after equilibration with oxygen. In no experiment was the oxygen content of the oxides after equilibration found to be in excess of the expected stoichiometric concentrations, and the X-ray data revealed no structures other than NiO and Fe_2O_3.

For nickel monoxide in particular the present result is more acceptable than the previously suggested oxygen excess of 0.07, since excess oxygen concentrations of only 0.006 in CoO at 950° C and 0.04 in FeO at 600° C correspond to the oxygen-rich phase boundary of the monoxides [9, 10]. If the defect interaction energies [9, 11] in FeO, CoO and NiO represent the important parameters involved in bringing about phase-transition in the monoxides, then the maximum permitted oxygen excess in the three oxides on the oxygen-rich phase-boundary should decrease in the order FeO $>$ CoO $>$ NiO, and in the case of nickel monoxide only be attained at very high oxygen pressures at these temperatures.

References

1. C. C. ADDISON, B. F. G. JOHNSON, and N. LOGAN, *J. Chem. Soc.* (1965) 4490.
2. R. ROY, *Bull. Soc. Chim.* (1965) 1065.
3. D. P. BOGATSKY, *Zhur. obshchei Khim.* **21** (1951) 3.
4. D. P. BOGATSKY and V. MINEYEVA, *Fiz. Tverd. Tela. Akad. nauk SSSR Sbornic Statei* **2** (1959) 361.
5. D. P. BOGATSKY and V. MINEYEVA, *Zhur. obshchei Khim.* **29** (1959) 1358.
6. A. N. KUZNETSOV, *Zhur. neorg. Khim.* **13** (1968) 2077.
7. C. S. HOLTERMANN, *Ann. Chim* **14** (1940) 122.
8. S. P. MITOFF, *J. Chem. Phys.* **35** (1961) 882.
9. J. T. COX and C. M. QUINN, *J. Mater. Sci.* **4** (1969) 33.
10. A. MUAN, *Amer. J. Sci.* **256** (1958) 171.
11. J. S. ANDERSON, *Proc. Roy. Soc.* **A185** (1946) 69.

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R. W. DRAKEFORD*
C. M. QUINN†
Inorganic Chemistry Laboratory
The University of Oxford, UK

On the Measurement of the Surface Energy of Solids

In *J. Mater. Sci.* **5** (1970) 351 a paper on the bubble technique for the measurement of the surface energy of solids was published. The theory of the measurement and equation 4 used for calculating surface energy γ from the observations is easily shown to be erroneous. It assumes that the high-pressure gas present in the bubbles causes no strain and no stress in the surrounding metal. This assumption cannot be accepted.

(1) In many instances "the bubbles were faceted" that is, the gas-solid interface was plane. No capillary pressure acts across plane interfaces. Hence, in these experiments, the whole gas pressure was balanced by the compression stresses in the solid. Nevertheless, some values for γ were deduced from these observations also.

(2) In some similar systems, "swelling and warping" takes place. It is not stated whether any such deformation was noticed in the irradiated copper. If a deformation was present, the stresses caused by it counteracted the pressure in the bubbles. If the deformation was negligible, that is the external volume of the solid did not change in spite of the formation of bubbles in it, then the solid material was under a compressive stress, and this stress acted against the gas pressure.

The surface energy of solids cannot be determined by the bubble technique as it cannot by any other method so far devised [1, 2].

References

1. J. J. BIKERMAN, *Phys. Stat. Sol.* **10** (1965) 3; **12** (1965) K 127.
2. *Idem*, "Physical Surfaces" (Academic Press, New York, 1970), p. 202.

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J. J. BIKERMAN
15810 Van Aken Blvd.
Cleveland, Ohio 44120, USA

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*Now with Urquhart-Dykes and Lord, Columbia House, 69 Aldwych, London, EC2.

†Now at Department of Physical Chemistry, The University, Birmingham.

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