

### Orientation of Oxide Films on Iron

SINCE the publication of a previous note on the orientation of FeO (wüstite) films on  $\alpha$ -iron<sup>1</sup>, the complete series of oxide layers on iron has been studied. In the X-ray photographs of the FeO films on single crystals of iron, some reflections were identified as coming from Fe<sub>3</sub>O<sub>4</sub>, resulting from the partial decomposition of the wüstite phase. The pattern showed that this Fe<sub>3</sub>O<sub>4</sub> was identically oriented with the FeO, with all planes of the same indices in the two cubic lattices parallel. The same orientation relationship held when an FeO film was grown by reduction on a large natural crystal of magnetite (Fe<sub>3</sub>O<sub>4</sub>).

Plots of the atom arrangement on the interfacial crystallographic planes of the Fe, FeO, and Fe<sub>3</sub>O<sub>4</sub> lattices show that the orientation relationships described above are quite reasonable when considered on the basis of matching of atom positions. In the Fe and FeO lattices, the geometric configurations of the iron atoms on the matching cube planes are identical, and the spacings agree to within six per cent. In the matching cube planes of the FeO and Fe<sub>3</sub>O<sub>4</sub> lattices, the configurations of the iron atoms in the two are nearly identical, and those of the oxygen atoms are exactly so, with the interatomic spacing agreeing to within about three per cent.

The orientation relationships existing in overgrowths of Fe<sub>3</sub>O<sub>4</sub> with Fe<sub>2</sub>O<sub>3</sub> were reported many years ago by a number of mineralogists as consisting in a parallelism of the basal hexagonal plane of the hematite and the octahedral plane of the magnetite, with the [110] direction in the match plane of magnetite normal to the [10·0] direction in that of hematite. Grüner<sup>2</sup> has studied this relation, and concludes that the oriented 'intergrowth' is made possible by the sharing of one oxygen plane by both crystals. This theory is in complete accord with the FeO-Fe<sub>3</sub>O<sub>4</sub> orientations found in the present work. It is interesting that the oxygen atoms determine the orientation relationship in the case of Fe<sub>2</sub>O<sub>3</sub> on Fe<sub>3</sub>O<sub>4</sub>, and iron atoms in the case of FeO on Fe, while the two possibilities would produce the same result in the intermediate case of Fe<sub>3</sub>O<sub>4</sub> with FeO.

In 1922, Tammann<sup>3</sup> suggested that fixed orientation relationships between a polycrystalline metal and its adhering oxide layer would, by controlling the orientation of the oxide layer on each grain, lead to differences in the rate of oxidation from grain to grain, on the basis that diffusion through the oxide lattice is anisotropic. But though diffusion must take place by the movement of atoms from one lattice point to another and is thus anisotropic on a microscopic scale, it cannot be anisotropic on a macroscopic scale if the lattice is cubic, as demonstrated by calculations by the authors based on lattice symmetry considerations. All the existing experimental data show that diffusion in cubic metals is isotropic, as pointed out by Mehl in a recent lecture<sup>4</sup>. Although more or less self-evident, the calculations showed that diffusion in non-cubic lattices is not necessarily isotropic. To eliminate the effect of possible anisotropic diffusion through the thin external layer of hexagonal Fe<sub>2</sub>O<sub>3</sub>, specimens of high-purity iron were oxidised to the temper colour stage by heating in a hydrogen-water vapour atmosphere corresponding to the Fe<sub>3</sub>O<sub>4</sub> phase field on the equilibrium diagram of Emmett and Shultz<sup>5</sup>; differences in rates of oxidation on different faces were again exhibited even though cubic oxide alone was formed. It is possible that the explanation of this phenomenon lies in the distortion

of the oxide lattice at and close to the interface, caused by a tendency of lattices which match imperfectly mutually to adjust their lattice spacings, like that found by Finch and Quarrell<sup>6</sup> for zinc oxide films on zinc.

Fixed oxide-metal orientation relationships may also provide the explanation of the observed discontinuity of the rate of oxidation of iron at the *A*<sub>3</sub> point<sup>7</sup>. Since the oxide lattices themselves undergo no transformation at this temperature, the rate at which oxygen is supplied to the oxide-metal interface should not vary discontinuously with temperature. It seems reasonable to suppose that the abrupt changes in oxidation rates result from the substitution of the crystallographic mechanism of oxidation of  $\gamma$ -iron for that of  $\alpha$ -iron.

R. F. MEHL.

E. L. McCANDLESS.

Metals Research Laboratory,  
Carnegie Institute of Technology,  
Pittsburgh, Pennsylvania, U.S.A.

<sup>1</sup> NATURE, 134, 1009 (1934).

<sup>2</sup> Amer. Mineralogist, 14, 223 (1929).

<sup>3</sup> Stahl u. Eisen, 42, 617 (1922).

<sup>4</sup> Annual Institute of Metals Lecture, Amer. Inst. Min. Eng. (1936).

<sup>5</sup> J. Amer. Chem. Soc., 52, 4268 (1930).

<sup>6</sup> NATURE, 131, 877 (1933).

<sup>7</sup> Fischbeck and Salzer, Metallw., 14, 733, 753 (1935).

### Hooke and his Editors

PROF. E. N. DA C. ANDRADE is to be congratulated in the interpretation of some of the more difficult passages in the manuscript Diaries of Robert Hooke (NATURE, March 7, p. 378). I hope that he may be equally successful with the entry for Dec. 28, 1689, which I have tentatively transcribed "DS com Mard to Counts".

But Prof. Andrade begins with the statement that Dr. Gunther "considers himself aggrieved" that Mr. Robinson was allowed to publish the part of the Diary belonging to the City of London. The reverse was the case. I was very pleased that anyone, and especially Mr. Robinson, should have secured permission to transcribe and publish it. Mr. Robinson, however, had himself informed me that permission to publish was not being given to him, but to the Royal Society, and Prof. Andrade can find evidence for this in a letter from the Guildhall Librarian to *The Times* of February 15 last year. I was aggrieved in 1930 because the Guildhall Librarian refused me permission to have a copy of the Diary made so that I could study it in Oxford, and I have been told that similar applications for studying the original manuscript are to be refused in future.

Still more misleading is Prof. Andrade's continuation, "it behoves us to examine a little Dr. Gunther's claim to have a right to be the editor of anything pertaining to Hooke". I have never made any such claim: on the contrary, I have invited others to edit his work. I have expressed indignation that his original manuscript materials should have been kept for so many years unknown and unknowable both to scholars and to the general public. Concealment happened in several ways: by part of his Diary being catalogued under the name of another author; by the binding of its pages in a wrong chronological order so that the first page, initialled by himself, came in the middle of the volume; by the refusal of owners to permit his manuscripts to be copied.

Through delay in publication, many valuable years have been lost and, what is even more regrettable,