

SHORT COMMUNICATIONS

CHANGES OCCURRING AT SURFACES DURING REACTIONS BETWEEN POWDERED IRON(III) OXIDE AND SOME CARBONATES

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Abstract

The spikes, platelets, and other features with extensive surfaces observed on the particles of the product of the reaction of barium carbonate with iron(III) oxide or aluminium oxide result from reaction with carbon dioxide in the atmosphere in the presence of water vapour. They do not appear to be features of the solid state reaction as was thought earlier.

It was reported earlier that the development of spikes, platelets, and other features with extensive surfaces are a feature of the reaction of barium carbonate with iron(III) oxide, in vacuum, to give BaFe_2O_4 .¹ Such features have not been observed in the analogous reactions between iron(III) oxide and strontium carbonate² or calcium carbonate,³ but were found in the products of reaction between barium carbonate and aluminium oxide.⁴

The formation of spikes and needles on the surfaces of solids reacting with one another seems highly significant regarding the mechanism, so a further investigation of the surfaces of grains of the products of reaction between the carbonates of barium, strontium, and calcium with iron(III) oxide and aluminium oxide with barium carbonate was undertaken using X-ray diffraction and electron microscopy.

Experimental

The materials and procedures were as reported before for the reactions of iron(III) oxide with barium,^{1,5} strontium,² and calcium carbonates.³

A few specimens were examined in a Cambridge Stereoscan scanning electron microscope after having been coated with a mixture of gold and palladium.

Results

When barium carbonate and iron(III) oxide reacted in vacuum the product immediately on removal from the vessel had a light greenish-brown colour and gave the X-ray diffraction pattern of orthorhombic BaFe_2O_4 ⁶ (see Fig. 1(a)). No spikes or

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¹ Beretka, J., Ridge, M. J., and Brown, T., *Trans. Faraday Soc.*, 1971, **67**, 1453.

² Beretka, J., and Brown, T., *Aust. J. Chem.*, 1971, **24**, 237.

³ Beretka, J., and Brown, T., *Aust. J. Chem.*, 1971, **24**, 1957.

⁴ Beretka, J., and Brown, T., unpublished data.

⁵ Beretka, J., and Ridge, M. J., *J. chem. Soc. (A)*, 1968, 2463.

⁶ Mitsuda, H., Mori, S., and Okazaki, C., *Acta crystallogr. (B)*, 1971, **27**, 1263.

other features could be found by electron microscopy. However, material that had been stored for 6–12 months in closed bottles was found to have lost its greenish colour, and gave a diffraction pattern quite different from that of the freshly prepared product (see Fig. 1(b)) and appeared to consist of poorly crystalline barium carbonate. When this brown material was examined by electron microscopy the grains were found to be coated with spikes similar to those reported earlier.¹

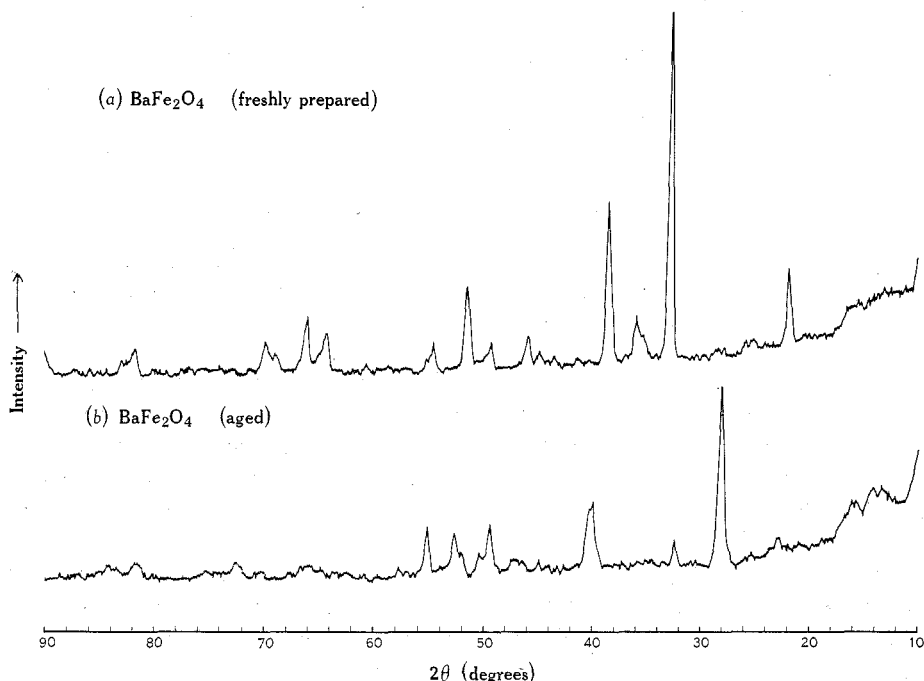


Fig. 1.—X-ray diffraction pattern of (a) freshly prepared BaFe_2O_4 (greenish colour), and (b) aged BaFe_2O_4 (brown colour). Conditions for X-ray diffraction: Co $K\alpha$ radiation at 40 kV, 12 mA, Fe filter; time constant 3.4 s.

To throw light on the changes undergone by BaFe_2O_4 after removal from the vacuum, a freshly prepared sample (light greenish-brown) was mixed with a few drops of water and the resulting paste let dry to constant weight in a conditioned room (20.5°C; 65% R.H.). After 6 hr the colour had become dark brown and the X-ray diffraction pattern had changed to that of the brown product (Fig. 1(b)).

A similar gradual transformation took place in a sample held at 100% R.H. at 20.5°C. The weight rapidly increased by about 30% and eventually by nearly 53%. Observations on the colour, weight, and X-ray diffraction pattern were accompanied by parallel examination by electron microscopy. It was evident that the spikes grew progressively, and were fully developed after about 10 days. Scanning electron micrographs (Fig. 2) of the transformed specimen showed that the grains were completely covered by spikes and other features with extensive surfaces.

Further investigation has shown that electron diffraction patterns of typical spikes could not be indexed with certainty in different orientations, but did not appear

to be due to BaFe_2O_4 as seemed to be the case previously.¹ Barium carbonate appeared to be indicated instead, although coincidence of the observed lattice parameters with those for this compound were not very good.

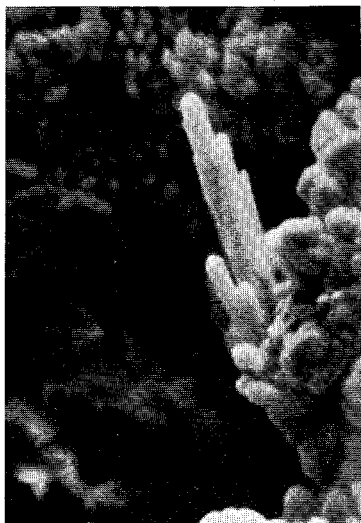


Fig. 2.—Scanning electron micrograph of the surface of the grains of well aged BaFe_2O_4 . Specimen coated with gold-palladium. Magnification, $9200\times$ on the screen.

In view of the indication of barium carbonate, some experiments were carried out to determine whether carbon dioxide was essential for the development of the features in question. A freshly prepared sample of BaFe_2O_4 was let stand in a $1/4$ atmosphere of water vapour in an enclosed system free from carbon dioxide. After 4 days a few minute spikes were visible, probably as a result of traces of carbon dioxide. X-ray diffraction showed that the material was virtually unchanged. The same period of time in the atmosphere would have resulted in considerable changes.

Samples of SrFe_2O_4 and CaFe_2O_4 underwent no changes in humid atmospheres. However, when freshly prepared BaAl_2O_4 (prepared at 900°C) was exposed to 100% R.H. in a desiccator, spikes, etc. developed on the grains and the X-ray diffraction pattern changed to one similar to Figure 1(b).

Conclusions

The spikes observed on the particles of the product of the reaction of barium carbonate with iron(III) oxide or aluminium oxide result from reaction with carbon dioxide in the atmosphere in the presence of water vapour. They do not appear to be a feature of the solid state reaction as was thought to be the case earlier.¹ The difficulties in indexing the electron diffraction patterns indicate that the product is in a distorted form. In view of the low temperatures at which the product forms, processes at surfaces are probably involved.

Acknowledgments

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