Solubility of calcium oxide in barium hexaferrite

In a previous paper [1], the isothermal section at 1100° C for the system $BaO-CaO-Fe_2O_3$ was reported. The most interesting result of that work was the determination of the solubility extent of calcium oxide in the barium hexaferrite network. In order to correlate this phenomenon with the properties of $BaO \cdot 6Fe_2O_3$ (magnetic properties, electrical conductivity, sintering kinetics) the boundaries of the single-phase region were determined with particular accuracy.

The starting materials were reagent-grade $CaCO_3$, $BaCO_3$ and Fe_2O_3. Calculated proportions of the powdered materials (Table I) were weighed, homogenized for 4 h with a mechanical mixer using ethanol as the dispersing agent; after drying, the mixtures were pressed into cylinders and prefired in air at 1000 ± 10° C for 24 h on a platinum holder in a resistance furnace. After quenching, the material was reground, pressed again into discs and air-fired at 1100 ± 10° C for 200 h. Polished sections of the quenched samples were examined by reflected light microscopy and by X-ray powder patterns taken with a Guinier De-Wolff camera. The radiation used was $CuK\alpha_1$.

A number of compositions were prepared along the joints between barium hexaferrite and hypothetical compounds $CaOxFe_2O_3$ with $x = 6, 5.5, 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1$. The general formula of these series was $A BaO \cdot 6Fe_2O_3 + B CaOxFe_2O_3$ with $A + B = 1$.

Examination of optical samples and diffraction patterns showed the presence of a triangular shaped single-phase region, with the longest side lying on the join $BaO \cdot 6Fe_2O_3-CaO \cdot 5.5Fe_2O_3$ (Fig. 1). The end member of the solid solution within this line is close to composition 5, whereas compositions 6, 7 and 8 exhibit a three-phase equilibrium.

With values of x below 5.5, lower solubilities of calcium oxide in barium hexaferrite were found, e.g. on the join $BaO \cdot 6Fe_2O_3-CaO \cdot 4Fe_2O_3$ the end member of the solid solution is very close to composition 17 (general formula $0.90BaO \cdot 6Fe_2O_3 + 0.10CaO \cdot 4Fe_2O_3$), on the join $BaO \cdot 6Fe_2O_3-CaO \cdot 2Fe_2O_3$ it is close to composition 32 (general formula $0.95BaO \cdot 6Fe_2O_3 + 0.05CaO \cdot 2Fe_2O_3$).

TABLE I Mol% prepared mixtures. For location refer to Figs. 1 and 2

Specimen	BaO	CaO	Fe_2O_3
1	12.14	2.15	85.71
2	10.00	4.29	85.71
3	7.14	7.14	85.71
4	10.22	4.38	85.40
5	9.52	5.13	85.35
6	8.82	5.88	85.29
7	8.12	6.64	85.24
8	7.41	7.41	85.18
9	13.04	1.45	85.51
10	12.41	2.19	85.40
11	11.77	2.94	85.29
12	10.45	4.48	85.07
13	7.69	7.69	84.62
14	11.94	2.99	85.07
15	10.68	4.58	84.73
16	8.00	8.00	84.00
17	13.24	1.47	85.29
18	12.69	2.24	85.07
19	11.68	3.70	84.62
20	10.94	4.69	84.37
21	8.33	8.33	83.33
22	11.20	4.80	84.00
23	8.69	8.69	82.61
24	13.87	0.73	85.40
25	13.43	1.49	85.08
26	12.98	2.29	84.73
27	11.47	4.92	83.61
28	9.09	9.09	81.81
29	13.92	0.73	85.35
30	11.77	5.04	83.19
31	9.52	9.52	80.95
32	13.97	0.74	85.29
33	13.63	1.52	84.85
34	13.28	2.34	84.38
35	12.07	5.17	82.76
36	10.00	10.00	80.00
37	12.39	5.31	82.30
38	10.53	10.53	78.95
39	12.73	5.45	81.82
40	11.11	11.11	77.78
41	14.49	0.47	85.04
42	17.20	0.90	81.90
43	15.43	1.64	82.93
44	14.50	5.50	80.00
45	16.66	16.66	66.66
46	12.50	25.00	62.50
47	20.00	20.00	60.00

The diffraction patterns of compositions lying on the join $BaO \cdot 6Fe_2O_3-CaO \cdot 5.5Fe_2O_3$ showed an appreciable distortion of the lines. In order to evaluate this distortion, the cell parameters of barium hexaferrite and composition 5 were calculated and refined by the least squares method [2].

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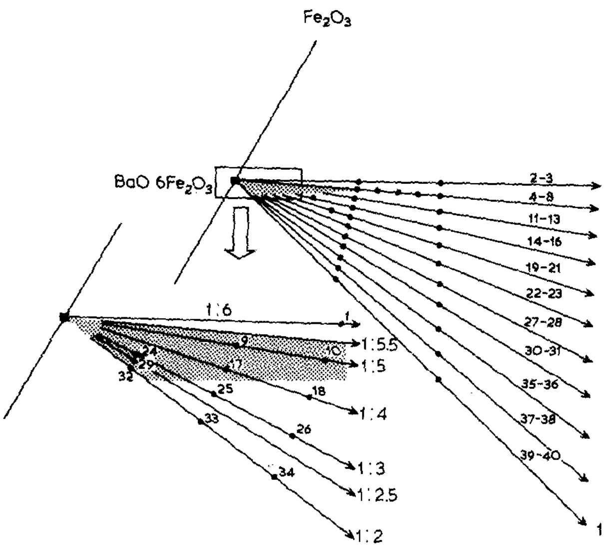

Figure 1 Location of compositions in the barium hexaferrite zone: shaded area = single-phase region.

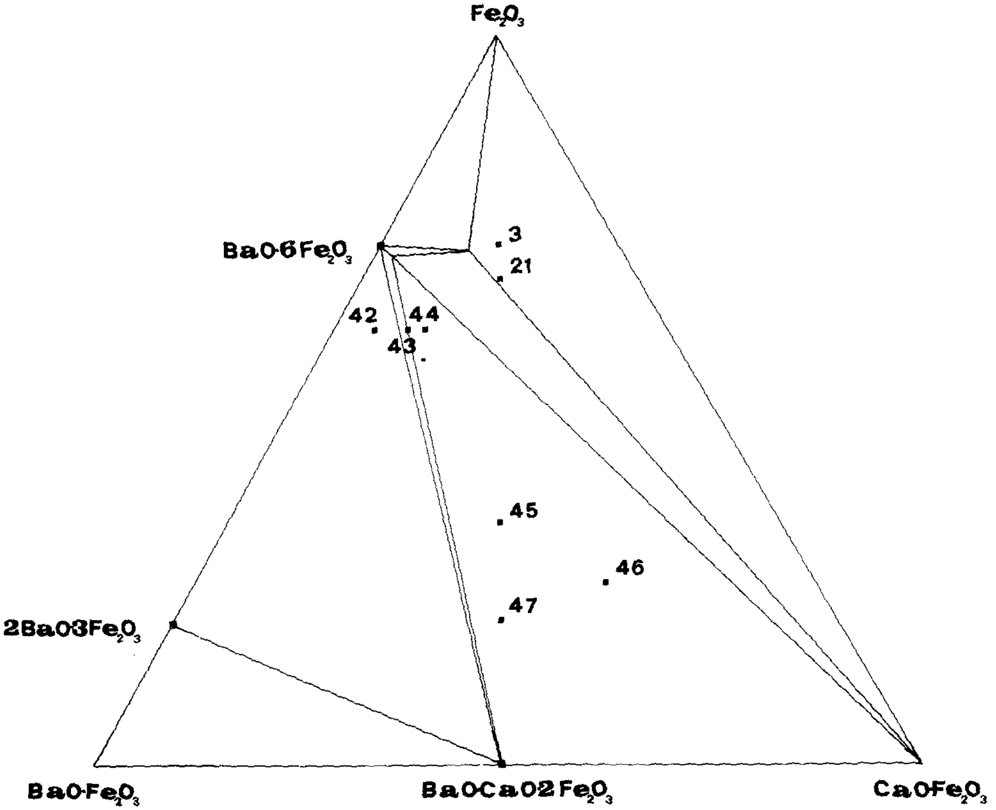

Figure 2 General view of the diagram Fe_2O_3–$BaO \cdot Fe_2O_3$–$CaO \cdot Fe_2O_3$, showing the location of compositions and the boundary lines of the two-phase and three-phase regions.

Ten reflections of each Guinier De-Wolff powder pattern were chosen, with $Pb(NO_3)_2$ as the internal standard.

Lattice parameters of hexagonal barium hexaferrite were found to be $a = 5.907$, $c = 23.187$, in agreement with reported single-crystal data [3]. The lattice parameters of composition 5 were found to be $a = 5.904$, $c = 23.154$.

Examination of the diffraction patterns of the other samples in the single-phase region was not indicative of any distortion of the cell parameters. No appreciable solubility was found along the join $BaO \cdot 6Fe_2O_3$–$CaO \cdot Fe_2O_3$. In all the samples of that line, the presence of three phases was determined: barium hexaferrite-type solid solution, calcium monoferrite and barium calcium ferrite. Examination of compositions 3, 8, 13, 16, 21, 42, 44, 45, 46, 47 and other compositions of the previous work [1] permitted two further ternary fields to be determined (see Fig. 2).

Adjacent to the single-phase region, three single pseudobinary fields are formed, with iron oxide, calcium monoferrite and barium calcium ferrite as the equilibrium phases (see Fig. 2).

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ELIO LUCCHINI
GIORGIO SLOKAR
Istituto di Chimica Applicata e Industriale,
Università di Trieste,
Italy

Diffusion in some iron-based metallic glasses

Iron-rich metallic glasses have been reported to crystallize by primary crystallization of α-iron followed by polymorphous crystallization of Fe_3B. The diameter of the α-iron crystals in $Fe_{86}B_{14}$ alloys obeys a √time-law [1, 2]. This parabolic relationship indicates that the growth is controlled by volume diffusion, and it should be possible to calculate diffusion data from primary crystallization. The aim of this communication is to discuss such an indirect method for predicting diffusion coefficients from primary crystallization data in more detail and to present first results from some iron-based metallic glasses.

For precipitation in supersaturated solid solutions Aaron *et al.* [3] calculated the radius r of spherical particles in volume diffusion-controlled particle growth to be proportional to √ time such that

$$r = \alpha\sqrt{(Dt)}, \qquad (1)$$

where α is a dimensionless parameter evaluated from the compositions at the particle interface and the composition of the sample and D is the diffusion coefficient. Knowing α and the particle radius, the diffusion coefficient can be estimated. Using this approach and assuming boron concentrations of about 1 at% in the primary α-iron crystals and about 25 at% at the crystal/amorphous interface (this concentration is indicated by the polymorphous crystallization of the matrix into Fe_3B), it is calculated that for $Fe_{86}B_{14}$ alloys $\alpha = 2$, for $Fe_{84}B_{16}$ $\alpha = 1.6$ and for $Fe_{80}B_{20}$ $\alpha = 1.0$.

Fig. 1 shows diffusion rates* estimated by this method versus temperature for these three Fe–B alloys (nominal composition). Within the accuracy of our measurements the diffusivity is independent of boron concentration at least for the temperature and concentration range so far investigated. At

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*Older data [2], indicating a boron-dependent diffusion coefficient, were calculated with a concentration-independent $\alpha = 2$ in Equation 1. These data are included in Fig. 1, but recalculated using the exact numbers of α.

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