

PRECIPITATION OF THE PHASE  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> IN GLASSES  
OF THE SYSTEM  $x$  Fe<sub>2</sub>O<sub>3</sub> PbO.2B<sub>2</sub>O<sub>3</sub> (\*)  
(0.1  $\leq$   $x$   $\leq$  0.6)

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**ABSTRACT** — The precipitation of the phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in glasses of the system  $x$  Fe<sub>2</sub>O<sub>3</sub> PbO.2B<sub>2</sub>O<sub>3</sub> depends both on concentration and cooling rate. It is shown that the effect of the cooling rate is strikingly important.

## 1 — INTRODUCTION

With glasses  $x$  Fe<sub>2</sub>O<sub>3</sub> PbO.2B<sub>2</sub>O<sub>3</sub>, the phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> does not precipitate for  $x < 0.3$ . From  $x \geq 0.3$  the phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> begins to precipitate and this effect becomes more and more intense with the increase in  $x$ . The effect of the cooling rate is preponderant. Experiments were devised in order to get experimental evidence of the influence of the factors that determine the precipitation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

## 2 — THE ROLE OF THE COOLING RATE

The cooling rate depends on a number of factors such as thermal diffusivity, radiation transfer, geometric shape, surface conditions and first of all on the sample volume. In the next paragraph is described that blocks of glass with considerable

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dimensions were prepared so that a rather smooth variation of cooling rate was obtained between the central zone and the walls. So, it was possible to observe the influence of the cooling rate on the precipitation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

### 3 — OBSERVATIONS WITH GLASSES $x\text{Fe}_2\text{O}_3 \cdot \text{PbO} \cdot 2\text{B}_2\text{O}_3$

#### 3.1 — *Glass preparation*

The constituents of the glass (Fe<sub>2</sub>O<sub>3</sub>, PbO, BO<sub>3</sub>H<sub>3</sub>) were mixed in stoichiometric proportions during several hours in a «rotary ball mill». The mixture was put inside a platinum crucible that was introduced in a furnace at 1100°C during 2 hours. The liquid was afterwards moulded. The mould was pre-heated and was formed by metallic blocks that were adequately disposed. The blocks were recovered by colloidal graphite. The so prepared glass clocks had approximately 6 cm × 4 cm × 2 cm. They were introduced in a furnace at 450°C for annealing (2 hours). Glasses were prepared corresponding to the following compositions:  $x = 0.1, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.48, 0.5, 0.52, 0.55, 0.57, 0.6$ .

#### 3.2 — *Observation of the glass structure*

The blocks of glass were sliced and several sections were chosen for mounting and polish.

For  $x = 0.1$  and  $0.2$ , the optical microscope, the scanning electron microscope and the X-rays did not reveal the presence of the phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

The first observed crystals began to appear for  $x = 0.3$ , close to the surface of the sample. Fig. 1 and Fig. 2 show photographs corresponding to compositions  $x = 0.3$  and  $x = 0.35$  obtained with the scanning electron microscope. All the other photographs were obtained with the same apparatus.

For  $x = 0.4$ , zones with crystals were observed in the bulk of the material (Fig. 3), but X-rays did not reveal yet the presence of the phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

The peaks corresponding to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by X-rays diffraction only appear for  $x \geq 0.45$ , because in these conditions the con-

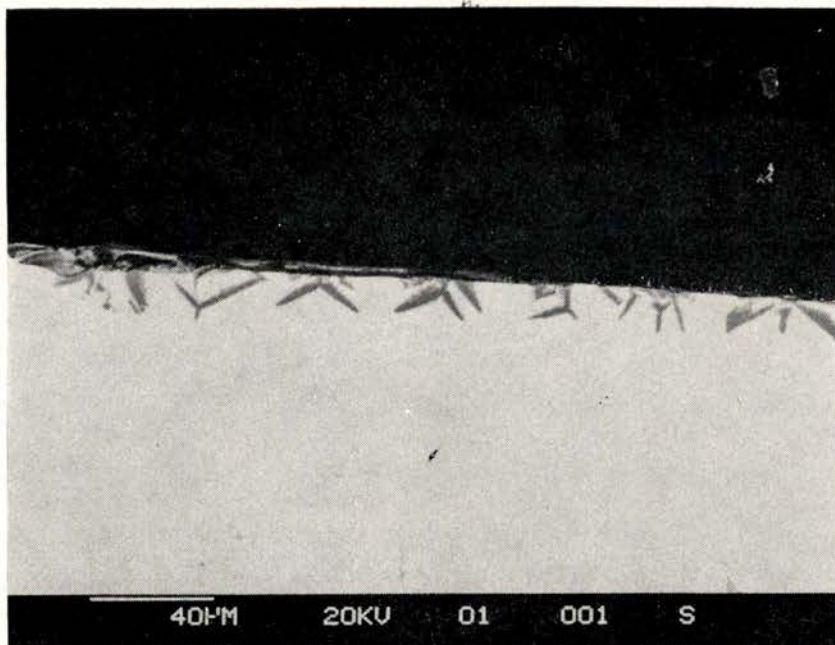


Fig. 1 — Small crystals are formed at the surface of the sample  
( $x = 0.3$ ) ( $\times 400$ )

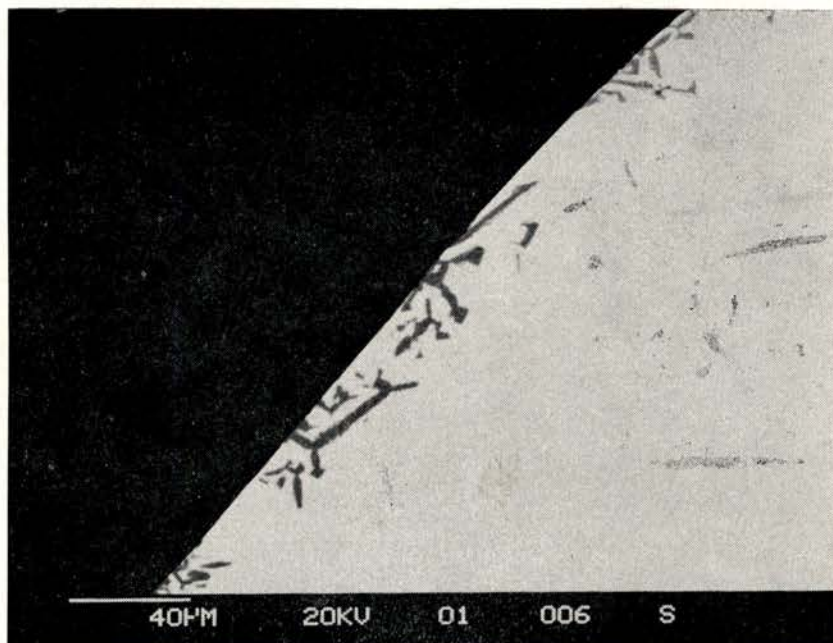


Fig. 2 — Crystal and aggregates close to the surface are bigger than in Fig. 3  
( $x = 0.35$ ) ( $\times 400$ )



Fig. 3 — An «island» formed by crystals is seen, but the overall concentration is very small and X-rays do not «see» the crystals  
( $x = 0.4$ ) ( $\times 200$ )

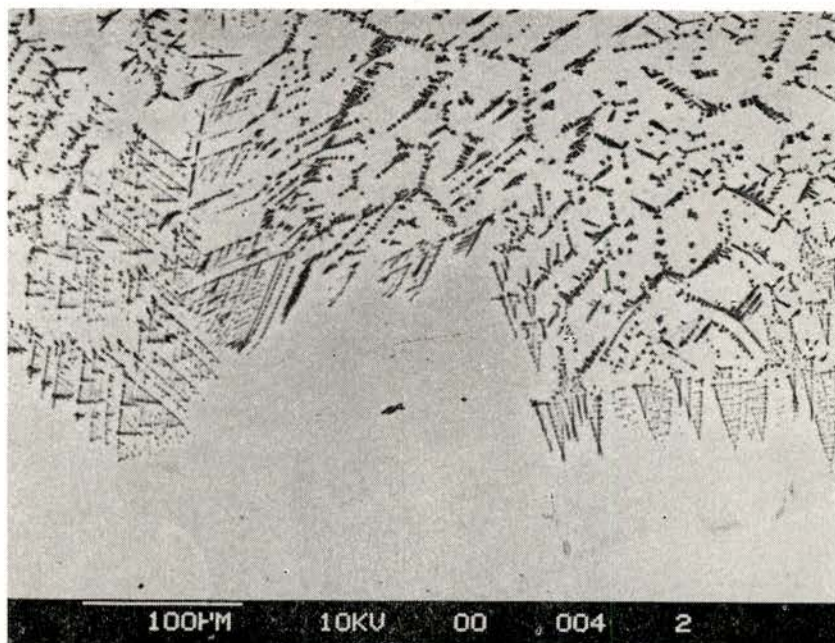


Fig. 4 — Here is shown the disappearance of crystals near the wall  
( $x = 0.5$ ) ( $\times 200$ )

centration of the phase becomes high enough. Nevertheless, no volume fraction determinations were possible for  $x < 0.48$ , due to the existence in the sample of regions with no crystals whose dimensions were very difficult to estimate.

For  $0.48 < x < 0.6$  it was observed that the volume fraction of the phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> increases rather regularly with  $x$ ; for a given  $x$ , the sizes of the crystals and crystal aggregates and the volume fraction increase from the boundary to the central zone of the sample.

Near the walls one observes no precipitation of crystals at all. The high cooling rate in these zones prevents entirely the crystallization (Fig. 4).

For  $x = 0.5$  and  $x = 0.6$  photographs of corresponding zones in the samples do not reveal an evident difference (Fig. 5, Fig. 6). Nevertheless repeated measurements have led to the result that the volume fraction is bigger for  $x = 0.6$ :

Composition $x$	Volume fraction	
	Central zone	zone far from centre (~ 1.5 cm from wall)
0.5	28 %	13 %
0.6	28 %	18 %

Intermediate values were found  $0.5 < x < 0.6$ . An absolute indetermination of 2 % is admitted in all results, due to the poor reproducibility of the conditions of sample preparation, difference in the mass of the sample from case to case and the errors inherent to the process of measurement.

It is well known that the morphology of the phases resulting from a demixtion process vary according the mechanism of the decomposition. In the case of the nucleation and growing mechanism the separated particles have a spherical appearance and show a poor connectivity. This is not evidently the case under study. The features of the precipitated phase that shows an irregular configuration and strong aggregation of the crystallites suggest the occurrence of a spinodal decomposition [1].

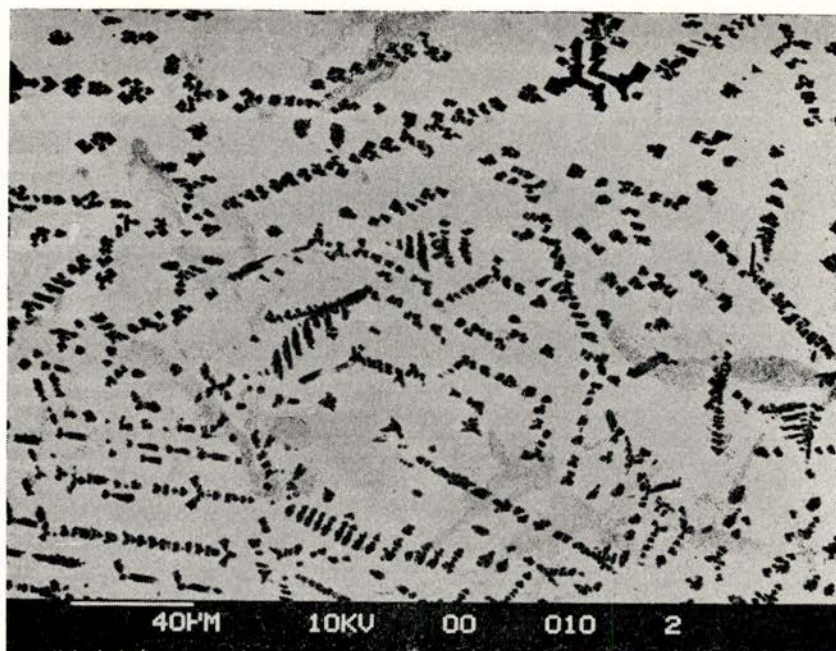


Fig. 5— This is a region of small crystals, not too far from the wall. Crystals are spread all over the sample ( $x = 0.5$ ) ( $\times 400$ )

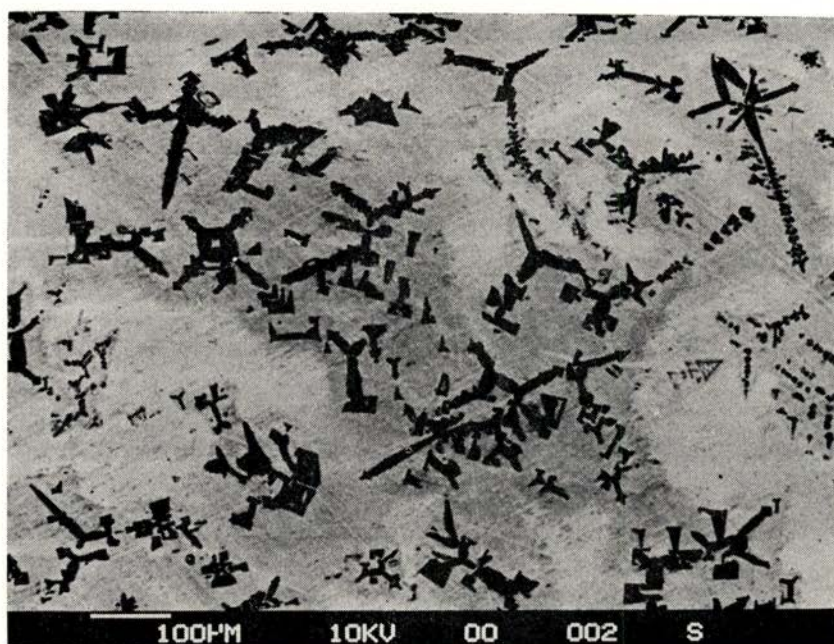


Fig. 6— This is a central zone. In general the crystals constitute big and irregular aggregates ( $x = 0.6$ ) ( $\times 100$ )

The technique used for volume fraction determination [2, 3] was point counting. Measurements were carried on with a transparent millimetric sheet, where a mesh of adequate size (of the same order of that of the crystallites) was chosen.

#### 4 – CONCLUSION

The precipitation of the phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in glasses of the system  $x\text{Fe}_2\text{O}_3 \cdot \text{PbO} \cdot 2\text{B}_2\text{O}_3$  is strongly dependent on the cooling rate. Regions where the cooling rate is high enough (vicinity of walls) are completely devoid of crystals. On the other hand, big aggregates of crystals appear in central zones where the cooling rate is minimum. The volume fraction of the phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> increases with  $x$  ( $x \geq 0.3$ ).

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