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# Formation of pseudobrookite through gaseous chlorides and by solid-state reaction

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Pseudobrookite ($Fe_2TiO_5$) was prepared from $Fe_2O_3$–$TiO_2$ mixtures at 850 and 950 °C in air, argon and chlorine atmospheres. In the latter case, an experimental arrangement in which $Fe_2O_3$ and $TiO_2$ were placed in separated compartments under the same chlorine atmosphere was also used. Pseudobrookite was identified by X-ray powder diffraction and microstructurally characterized by scanning electron microscopy. The very different pseudobrookite morphologies in each atmosphere allow us to propose that the formation mechanism involves $Ti^{4+}$ diffusion in the $Fe_2O_3$ surface in air and argon atmospheres and vapour transport through $FeCl_3(g)$ and $TiCl_4(g)$ in the chlorine atmosphere.

## 1. Introduction

Pseudobrookite (PSB) crystallizes in the orthorhombic system (space group *Bbmm*), with cell dimensions $a = 0.9767$ nm, $b = 0.9947$ nm, $c = 0.3717$ nm [1]. Its structure, first described by Pauling [2], has metal ions in two crystallographic sites; one of them is a distorted octahedron (8f site) [3] and the other a rather symmetric octahedron (4c site) [3] of oxygens. The PSB is reddish brown to black and its habit is usually tabular and elongated, sometimes long prismatic or needle-like and striated.

The investigations in relation to PSB can be divided into three groups. In one group, study was stimulated by an interest in mineralogy [4, 5]. The second group of investigations was directed toward a systematic understanding of phase equilibrium in the system Fe–Ti–O, with emphasis on extractive metallurgy [5–12]. The third group focused on the PSB microstructure and associated properties, for example thermal expansion anisotropy and anisotropy spin glass behaviour [13–17].

Concerning mineralogy, the pseudobrookite-type minerals are relatively rare in igneous rocks [5, 18], most of those minerals deriving from oxidation–exsolution processes of magnesium-bearing haematite–ilmenite and ulvospinel–magnetite phases. The limited terrestrial occurrence of PSB can be explained by its thermodynamic instability at low oxygen fugacity, low temperature and high pressure. PSB is stable over 585 °C [18] at 1 bar, but this limit temperature increases rapidly with pressure. Thus PSB occurs in rocks of appropriate composition in an oxidizing environment at low pressure and high temperature. The alteration of ilmenite in nature is, in some aspects, analogous to high-temperature oxidation. For this reason, PSB also appears in the reaction products of the high-temperature ilmenite-beneficiation process. Karkhanavala and Momin [19] investigated the oxidation of natural ilmenite in air and concluded that the product of oxidation at 850 °C was a mixture of haematite, PSB and rutile. Bhogeswara Rao and Rigaud [20] investigated the oxidation of synthetic ilmenite in air, and the oxidation products identified above 900 °C were PSB and rutile. Grey and Reid [21] have produced PSB plus rutile by heating mixtures of $Fe_2O_3$ and $TiO_2$ in the molar ratio 1:2 above 800 °C. These authors have shown that the rate of formation of PSB below 800 °C is very slow. Haggerty and Lindsley [18] have shown, from hydrothermal studies, that PSB formation from ilmenite below 800 °C is very slow, which is in agreement with the observation of Gupta *et al.* [22].

In relation to the phase equilibrium in the system Fe–Ti–O, thermodynamic data are useful in understanding the formation of iron titanate ores and in controlling oxidation–reduction processes currently in use for the treatment of these ores. The Fe–Ti–O system has been studied [6–9], but a complete set of thermodynamic data is not yet available. The phase relations in air for the system iron–titanium oxide in air at temperatures close to the liquidus were determined by Mac Chesney and Muan [7]. Isothermal sections through the phase diagram of the system $FeO$–$Fe_2O_3$–$TiO_2$ at 1200 °C [8] and 1300 °C [9] has been reported, and the occurrence of the ternary solid solutions magnetite–ulvospinel ($Fe_3O_4$–$Fe_2TiO_4$), haematite–ilmenite ($Fe_2O_3$–$FeTiO_3$) and ferric–ferrous pseudobrookite ($Fe_2TiO_5$–$FeTi_2O_5$) has been described. 3 mol % $Fe_2O_3$ may be dissolved in $TiO_2$ at 1200 °C in air [8], before PSB appears. No

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composition range was reported for PSB. At 1300 °C in air [9], the limit of the rutile phase occurs at 96 wt% $TiO_2$ + 2.5 wt% $Fe_2O_3$ + 1.5 wt% FeO with $Fe^{3+}/Fe^{2+} = 1.5$. PSB was reported to have a composition range. Akimoto *et al.* [1] and Haggerty and Lindsley [18] have investigated the solid-solution series between PSB and $FeTi_2O_5$. On the other hand, little information has been given for the system $Fe_2O_3$–$TiO_2$ at temperatures below 1000 °C. Karkahnavala and Momin [6] have determined that the system $Fe_2O_3$–$TiO_2$ heated in air up to 1200 °C is a simple binary, without any solid solutions and with a single binary compound: $Fe_2TiO_5$ (pseudobrookite).

In relation to PSB microstructure and associated properties, mineral PSB is the prototype of a series of other phases that have the same structure: $Al_2TiO_5$, $MgTi_2O_5$, $Ti_3O_5$, etc. [4, 13, 21]. Some of these materials have become of interest after a high degree of thermal expansion anisotropy was reported. The expectation is that PSB would be useful as high-temperature ceramics due to a combination of high thermal shock resistance and good insulating capability.

In the present work, the synthesis and growth of PSB crystals from $Fe_2O_3(s)$–$TiO_2(s)$ powders mixture in air, argon and chlorine atmospheres was studied. The preparation methods of $Fe_2TiO_5$ are described and a mechanism for each atmosphere is proposed.

## 2. Experimental procedure

### 2.1. Materials

Starting samples were prepared by mixing $TiO_2$, which initially contained 95% anatase–5% rutile (Mallinckrodt Chemical Works, USA), and α-$Fe_2O_3$ (Spex Industries, Inc., USA) powders in molar ratio 1:1. The specific areas were 9.4 and 3.0 $m^2 g^{-1}$, respectively, as measured by nitrogen adsorption at 77 K (M 2205, Micromeritics Instrument Corp., Norcross, GA). The $TiO_2$ powder was composed of particles ranging from less than 1 μm to about 60 μm [23] (estimated by scanning electron microscopy: SEM 515, Philips Electronic Instruments). Fig. 1a shows that these particles were also agglomerates composed of very small grains which had a mean size of about 0.2 μm. The α-$Fe_2O_3$ powder had a particle distribution from less than 10 μm to about 200 μm (estimated by SEM) which in turn were (as shown in Fig. 1b) agglomerates composed of very small grains with a mean size of about 0.2 μm. Argon, 99.99% purity (AGA, Argentina), and chlorine, 99.8% purity (Indupa, Argentina) were used.

### 2.2. Procedure

In order to analyse the effect of the atmosphere on the reactivity in the system $Fe_2O_3$–$TiO_2$, starting samples were heated at 850 and 950 °C in air, argon and chlorine atmospheres for several hours (see Tables I and II). For treatment in air, starting samples were placed in open quartz crucibles and heated for 1 and 4 h at 950 and 850 °C and then quenched (runs 1–4). For the argon (runs 5–8) and chlorine (runs 9–17) atmospheres, starting samples were placed in capsules, which were held in vacuum ($1.3 \times 10^{-5}$ MPa) for 1 h until they were outgassed. Then argon or chlorine was injected and the capsules were sealed. The gas pressure was chosen so that a value of 0.021 MPa was obtained at room temperature. The encapsulated samples were then heated at the working temperature for the selected time, and finally quenched at room temperature.

The design of the capsules was different for each atmosphere. In argon, starting samples were placed in spherical capsules of 1 cm diameter (runs 5–8). For the

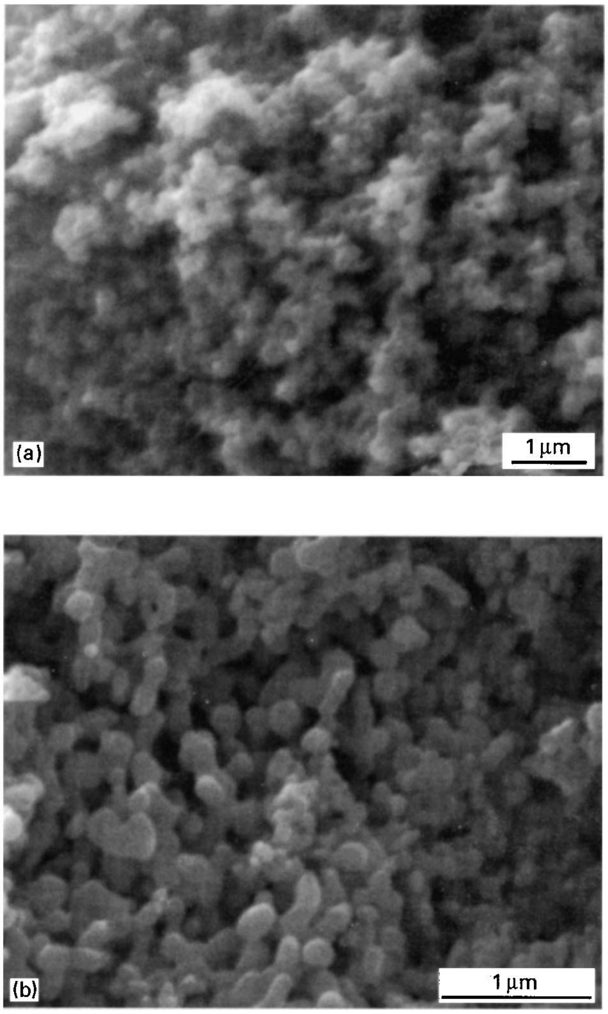

*Figure 1* (a) Surface morphology of a particle of $TiO_2$. (b) Surface morphology of a particle of $Fe_2O_3$.

TABLE I Phases detected by XRD after thermal treatment in air and argon atmospheres

| Run | Atmosphere | Temperature (°C) | Time (h) | Phases observed[a] |
|---|---|---|---|---|
| 1 | Air | 950 | 1 | R, H, PSB |
| 2 | | | 4 | R, H, PSB |
| 3 | | 850 | 1 | R, A, H |
| 4 | | | 4 | R, A, H |
| 5 | Argon | 950 | 1 | R, H, PSB |
| 6 | | | 4 | R, H, PSB |
| 7 | | 850 | 1 | A, R, H, PSB |
| 8 | | | 4 | R, H, PSB |

[a] A, anatase; R, rutile; H, haematite; PSB, pseudobrookite.

TABLE II Phases detected by XRD after thermal treatment in chlorine atmosphere

| Run | Samples used | Temperature (°C) | Time (h) | Phases observed[a] |
|---|---|---|---|---|
| 9 | Mixed oxides disposition | 950 | 1 | PSB |
| 10 | | | 4 | PSB |
| 11 | | | 24 | PSB |
| 12 | | 850 | 1 | R, H, PSB |
| 13 | | | 4 | R, H, PSB |
| 14 | Separated oxides disposition | 950 | 4 | (I)[b] R, PSB<br>(II)[b] H |
| 15 | | | 24 | (I) PSB<br>(II) H |
| 16 | | 850 | 4 | (I) R, PSB<br>(II) H |
| 17 | | | 24 | (I) PSB<br>(II) H |

[a] A, anatase; R, rutile; H, haematite; PSB, pseudobrookite.

[b] I and II indicate the compartment according to Fig. 2.

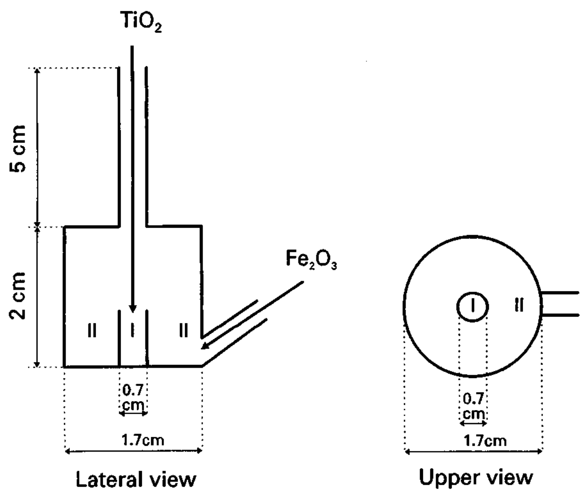

*Figure 2* Schematic drawing of a divided capsule used for treatment in chlorine. The different compartments are indicated as I and II.

experiments in a chlorine atmosphere, starting samples were placed in two types of quartz capsules (runs 9–17). The first one was the same type as that used in the argon atmosphere (runs 9–13). The second one (runs 14–17) had two cylindrical coaxial compartments (I and II) as depicted in Fig. 2 (termed a divided capsule). For runs 14–17, pure $TiO_2$ powder was placed in compartment I, while pure $Fe_2O_3$ powder was placed in compartment II. Two oxide dispositions were used: separated oxides in the divided capsule, and mixed oxides in capsules with $Fe_2O_3$–$TiO_2$ mixture.

A Philips X-ray diffractometer (PW 1710-01, Philips Electronic Instruments) was used to obtain X-ray powder diffractograms from samples after each heating treatment. Nickel-filtered Cu$K_\alpha$ radiation was used. Scanning electron microscopy and energy dispersive X-ray spectroscopy (EDXS) were used to characterize the microstructure of each phase developed after each thermal treatment.

## 3. Results

### 3.1. X-ray diffraction (XRD) studies

### *3.1.1. Treatments in air and argon*

A series of experiments, in which the $Fe_2O_3$–$TiO_2$ mixture was heated in air (runs 1–4) or argon (runs 5–8) atmospheres for 1 and 4 h at 850 and 950 °C was carried out. The XRD results are given in Table I. The phases detected on heating the starting samples in air for 1 h at 950 °C (run 1) were rutile ($TiO_2$, R), haematite ($Fe_2O_3$, H) and pseudobrookite ($Fe_2TiO_5$, PSB). At a longer heating time (4 h), no change in the present phases was observed. On heating the starting samples at 850 °C (runs 3 and 4), PSB phase was not detected, whereas the anatase ($TiO_2$, A) phase still remained [24]. The phases observed after heating samples in argon at 950 °C for 1 and 4 h were also R, H and PSB. In the starting sample heated for 1 h at 850 °C (run 7), the phases detected were A, R, H and PSB. Longer heating times at 850 °C (run 8) produced no further changes in the present phases, except a decrease in the anatase/rutile ratio. In all cases, the anatase transformed to rutile under the influence of the atmosphere and thermal treatment used, as has been shown in a previous study [24]. In the samples where PSB was formed, the colour changes on heating from white and red (titania and haematite, respectively) to brown (a mixture of PSB, haematite and titania).

### *3.1.2. Treatments in chlorine atmosphere*

Samples with mixed oxides disposition (runs 9–13) and those with separated oxides disposition (runs 14–17) were heated in chlorine for several hours at 850 and 950 °C. The crystalline phases remaining after each treatment are indicated in Table II. It can be seen that at 950 °C, for 1, 4 and 24 h heating (runs 9–11), PSB was the only identified phase. At 850 °C (runs 12 and 13), PSB was also detected but the reaction was not complete because other phases, such as R and H, remained. For runs 14–17, we found residual $Fe_2O_3$ in the outer compartment (number II); however, its initial amount was significantly diminished, as observed by simple inspection. In the central compartment (number I), the colour of the powder changed from white to brown and the phases detected were R and PSB (runs 14 and 16) or only PSB (runs 15 and 17). The A phase is absent after different treatments in a chlorine atmosphere, in agreement with the accelerating effect of that atmosphere on the anatase–rutile transformation [23].

### 3.2. SEM observations

To associate the PSB phase formed in different atmospheres with its corresponding morphology, electron imaging via SEM was used. In general, two different types of morphology were identified. The first morphology is observed in treatments in air and argon atmospheres, and is characterized by the fact that shells of PSB with small grains are formed over the haematite particles. This shell-like morphology is shown in Fig. 3a, in which EDXS analysis allowed

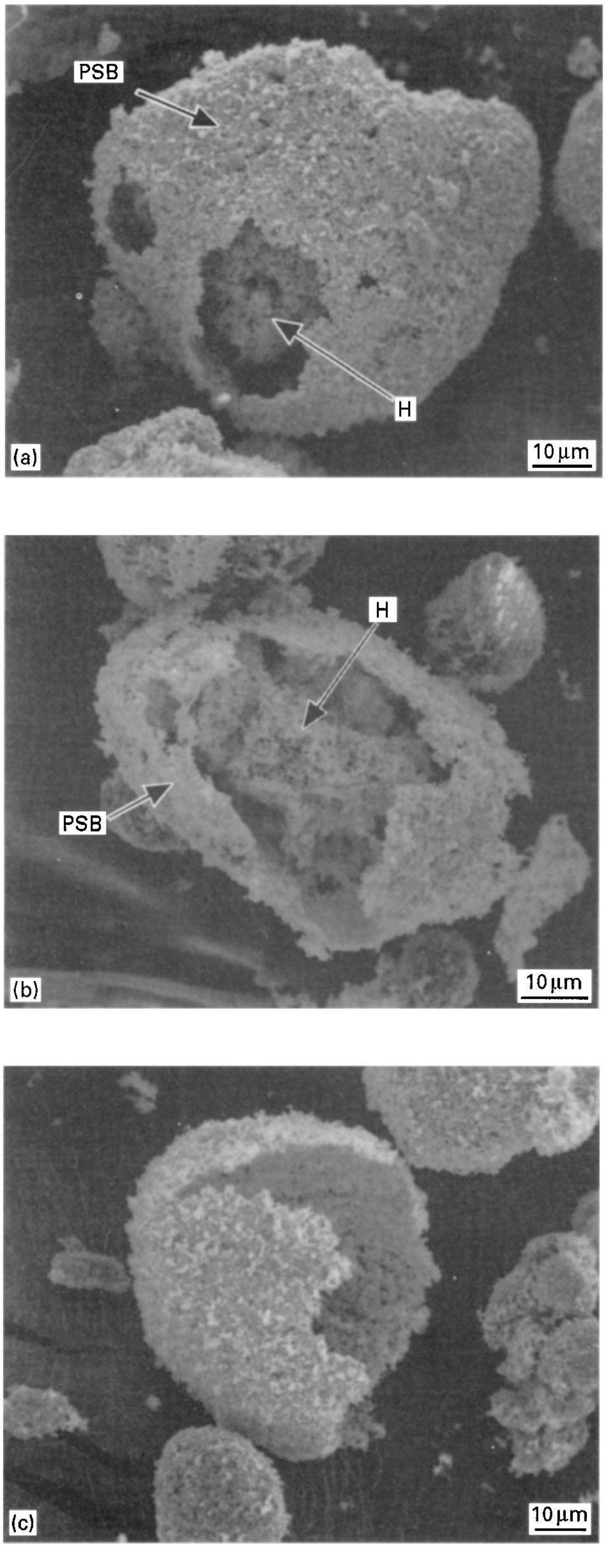

*Figure 3* Morphology of PSB shells obtained after heating $Fe_2O_3$–$TiO_2$ powder mixture in (a) air for 1 h at 950 °C, (b, c) argon for 1 h at 850 °C. PSB, pseudobrookite; H, haematite.

identification of several grains inside the shell as haematite. The PSB formed in argon is similar to that obtained in an air atmosphere, as shown in Fig. 3b and c (run 7). Fig. 3b shows a $Fe_2O_3$ particle surrounded by a PSB shell formed by grains of 0.2 µm mean size and Fig. 3c shows a free shell of PSB.

The second type of morphology is associated with the formation of huge PSB crystals with their typical crystalline habit in a chlorine atmosphere. The size and shape of PSB crystals differ from those formed in air and argon. In addition, the morphology of the PSB crystals obtained in chlorine depends upon the disposition of the $Fe_2O_3$ powder with respect to the $TiO_2$ powder. Fig. 4a shows crystals of PSB obtained at 950 °C (run 10), when $Fe_2O_3$ is mixed with $TiO_2$ (see Table II). These faceted tablet-shaped PSB crystals, about 10 µm long, were also observed in runs 9 and 11. At low temperature (850 °C), the PSB crystals are less faceted and non-uniform in size, ranging from 10–30 µm (see Fig. 4b). The shape of the crystals is tabular with some crystals being needle like. The small grains around the PSB particle correspond to the remaining rutile phase, as verified by EDXS analysis.

In runs 14–17, where pure $Fe_2O_3$ powder was separated from pure $TiO_2$ (see Table II), the PSB phase was obtained in the $TiO_2$ compartment (number II). Fig. 5a shows the crystals of PSB which consist of tablet-like faceted material grown on a $TiO_2$ particle (run 14, 950 °C). The mean grain size of $TiO_2$ (approximately 1 µm) was greater than the size of the starting pure $TiO_2$ powder, in agreement with previous results [23]. Detail of PSB crystals obtained from the same sample is shown in Fig. 5b. It can be seen that the size of these crystals is greater than 40 µm. At long heating times (run 15), the size of the crystals is about 0.6 mm long (Fig. 5c). Similar results were found for runs 16 and 17 heated at 850 °C (Fig. 6a and b). The size of crystals obtained after heating for 4 h is about 8 µm (see Fig. 6a) whereas for 24 h treatment, the size of PSB tablets is greater, about 20 µm (Fig. 6b).

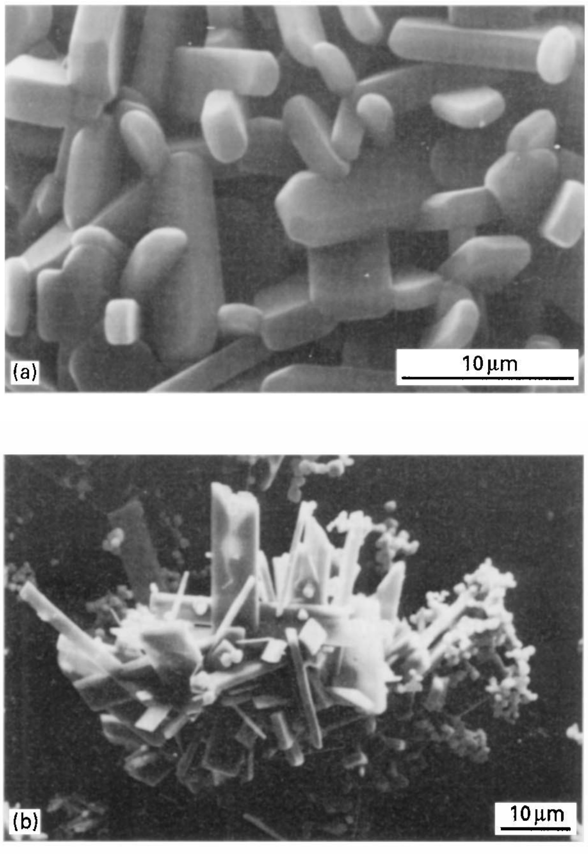

*Figure 4* PSB tablets obtained after heating in chlorine for mixed oxides disposition for 4 h, (a) at 950 °C, (b) at 850 °C.

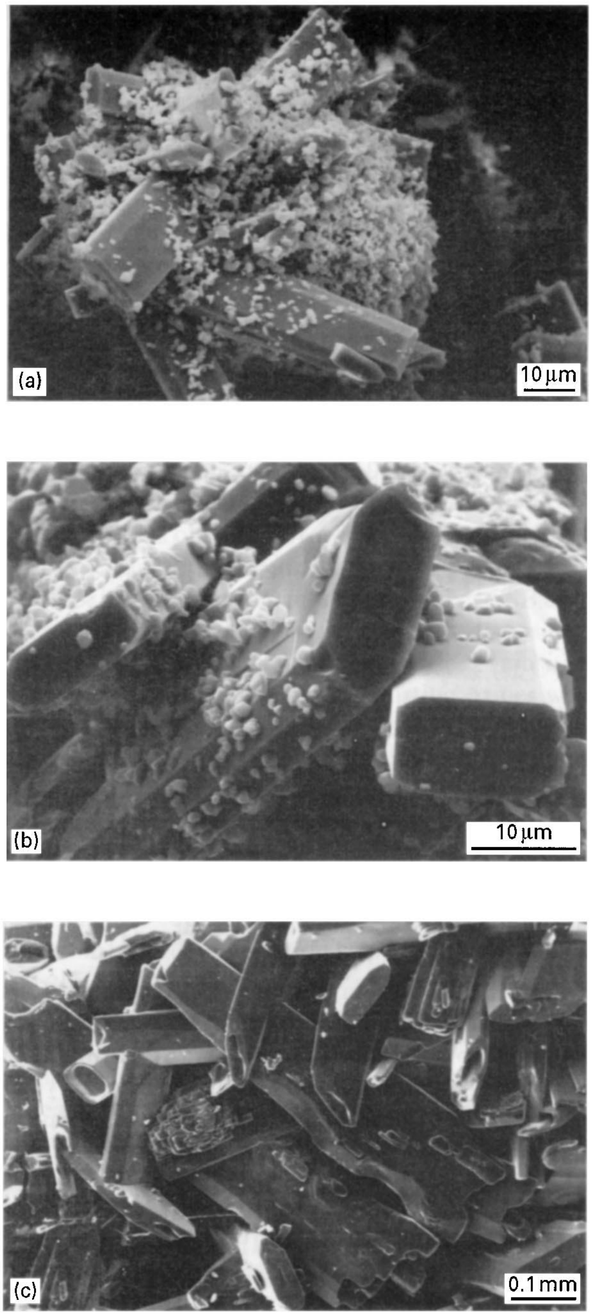

*Figure 5* PSB tablets obtained after heating in chlorine for separated oxides disposition at 950 °C, (a,b) 4 h, (c) 24 h.

An important observation is that the size of PSB tablets formed in chlorine for the mixed oxides disposition is approximately constant, irrespective of heating time. On the other hand, for the separated oxides disposition (experimental set up of Fig. 2), increasing the heating time in chlorine increases the size of PSB crystals.

## 4. Discussion

### 4.1. Formation of PSB in air and argon

In the present study, PSB ($Fe_2TiO_5$) obtained by heating a mixture of $Fe_2O_3$–$TiO_2$ in air and argon atmospheres (see Table I), was formed by the solid-state reaction described by the following equation

$$Fe_2O_3(s) + TiO_2(s) = Fe_2TiO_5(s) \qquad (1)$$

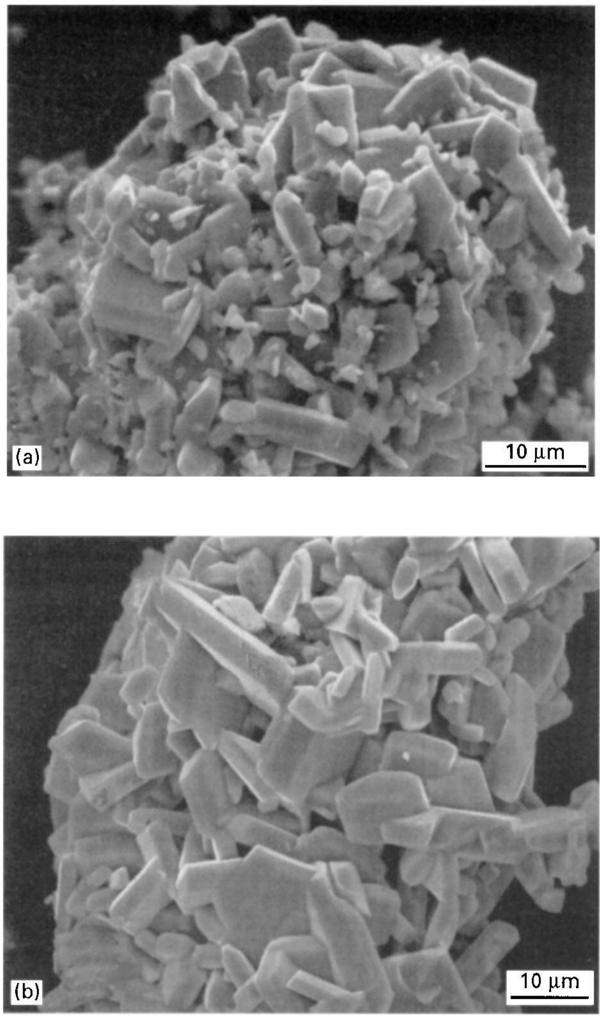

*Figure 6* Agglomeration of PSB crystals obtained after heating in chlorine for separated oxides disposition at 850 °C, (a) 4 h, (b) 24 h.

The SEM observations have shown that PSB was formed as a shell over $Fe_2O_3$ particles after a short heating time ($\approx 1$ h) at 950 °C (see Fig. 3a and b). Generally, during a solid–solid reaction, the product grows spherically from each contact point between reactants and, after a long time (10–100 h), the product zones overlap to form a shell, which advances from the outside toward the interior as the reaction proceeds [25]. In this stage, further progress of the reaction can only take place by a transport of the reactants through the shell of the product phase. Then, the reaction kinetic may be divided into two stages: the initial (before the shell formation) and the main stage. However, when the diffusion rate of the one component is much faster in the surface of the other component than in the bulk of the product, the initial stage of the reaction is not observed and diffusion through the product layer is rate-controlling [25]. Accordingly, fast PSB shell formation should indicate that the reaction mechanism is through a rapid titanium diffusion in the $Fe_2O_3$ surface. Moreover, this situation is supported by the low activation energy associated with the surface diffusion process in comparison with those of the bulk [26]. The isolated PSB shells and/or those surrounding a residual $Fe_2O_3$ particle (Fig. 3), even after long heating times (120 h), suggests (as mentioned) diffusion into the PSB as the reaction-controlling step. This mechanism of PSB formation must be encompassed with the diffusion of $Fe^{3+}$ from the $Fe_2O_3$ surface, where rearrangement of atoms in the outer layers of the crystal, surface vacancies and roughness, favour the dynamics of processes such as atomic diffusion. Despite the values of the $Ti^{4+}$ diffusion coefficient in PSB, as well as the $Ti^{4+}$ diffusion coefficient in $Fe_2O_3$ being unknown, the experimental evidence suggests that $Ti^{4+}$ diffuses rapidly on the surface of $Fe_2O_3$, forming PSB, and further diffusion across the PSB shell is the slow step.

Nevertheless, there is a difference in the behaviour of the oxides mixture in each atmosphere. The results in Table I reveal that an argon atmosphere favours the formation of PSB at temperatures (850 °C) lower than in an air atmosphere. This different behaviour can be interpreted by taking into account that the oxygen vacancies concentration in the metallic oxide lattice depends upon temperature and the partial pressure of oxygen in the reaction atmosphere. In an argon atmosphere, the oxygen partial pressure is approximately $10^{-6}$ MPa, which involves some degree of non-stoichiometry in $TiO_2$ [27] and $Fe_2O_3$ [28]. Based upon the fact that the atomic mobility increases in these non-stoichiometric oxides [26, 27], it is reasonable to expect an increasing $Ti^{4+}$ diffusivity. Therefore, the argon atmosphere enhances PSB formation with respect to air by favouring solid-state diffusion.

## 4.2. Formation of PSB in a chlorine atmosphere

In a chlorine atmosphere, PSB is also formed, but the shape and size of the crystals developed is very different from those obtained in argon and in air. The samples heated in argon or air atmospheres had small grains of PSB of undetermined shape. The samples heated in chlorine had high-faceted crystals of PSB with a defined tablet shape. There is a correlation between the PSB morphology and the kind of mass transport in each atmosphere. It is clear that the formation of PSB in air and argon requires contact between the oxides, and mass transport took place through solid-state diffusion. However, it is not possible to explain by this mechanism the formation and growth of PSB faceted crystals observed in a chlorine atmosphere, thus another mechanism through the gaseous phase should be involved.

In order to analyse the role of chlorine on the formation and growth of PSB crystals, the generation of gaseous species in the $Fe_2O_3(s)$–$TiO_2(s)$–$Cl_2(g)$ system must be considered. The thermodynamically most important reactions at the working temperature are

$$Fe_2O_3(s) + 3Cl_2(g) = 2FeCl_3(g) + 3/2\ O_2(g) \quad (2)$$

$$TiO_2(s) + 2Cl_2(g) = TiCl_4(g) + O_2(g) \quad (3)$$

for which the standard free energy changes, per mole of chlorine, as a function of absolute temperature, $T$, are given by [29]

$$\Delta G_2^\circ(\text{kJ mol}^{-1}) = -0.067\,38\,T + 99.31 \quad (4)$$

$$\Delta G_3^\circ(\text{kJ mol}^{-1}) = -0.028\,87\,T + 85.97 \quad (5)$$

This thermodynamic information allows calculation of the equilibrium pressures for gaseous species for coupled Reactions 2 and 3. The equilibrium pressures of $FeCl_3(g)$ and $TiCl_4(g)$ at 850 and 950 °C (see Table III) are high enough to generate an atmosphere of both chlorides to allow vapour mass transport between the grains of $Fe_2O_3$ and $TiO_2$. This possibility is in agreement with previous works [23, 30, 31] in which the role in mass transport of gaseous species formed in the interaction $TiO_2(s)$–$Cl_2(g)$ [23], $Fe_2O_3(s)$–$Cl_2(g)$ [30] and $Al_2O_3(g)$–$Cl_2(g)$ [31] was analysed.

Owing to the gaseous species formed by Reactions 2 and 3, the possible reactions for PSB formation at the working temperature are [29]

$$2FeCl_3(g) + TiCl_4(g) + 5/2O_2(g) \rightarrow Fe_2TiO_5(s) + 5Cl_2(g) \quad (6)$$

$$2FeCl_3(g) + TiO_2(s) + 3/2O_2(g) \rightarrow Fe_2TiO_5(s) + 3Cl_2(g) \quad (7)$$

$$Fe_2O_3(s) + TiCl_4(g) + O_2(g) \rightarrow Fe_2TiO_5(s) + 2Cl_2(g) \quad (8)$$

The standard free energy changes as a function of absolute temperature, $T$, for Reactions 6–8 are [29]

$$\Delta G_4^\circ(\text{kJ mol}^{-1}) = -461.30 + 0.25043 \quad (9)$$

$$\Delta G_5^\circ(\text{kJ mol}^{-1}) = -289.24 + 0.19264 \quad (10)$$

$$\Delta G_6^\circ(\text{kJ mol}^{-1}) = -163.73 + 0.04773 \quad (11)$$

from which Reaction 6 represents the thermodynamically most probable reaction. For samples with separated oxides disposition, the PSB formation is observed in the compartment in which $TiO_2$ was placed. Although this observation points to discarding the contribution of Reaction 7, the existence of huge PSB crystals indicates that titanium is also supplied by vapour transport, which is an experimental support that reinforces the idea that Reaction 6 is the main contribution to PSB formation. Therefore, iron and titanium are transported through $FeCl_3(g)$ and $TiCl_4(g)$, formed by Reactions 2 and 3, which in turn react in an oxygen surrounding atmosphere forming PSB crystals and regenerating chlorine, as indicated by Reaction 6.

The PSB formation requires experimental conditions that displace Equilibrium 6 to the right. This possibility can be evaluated from the degree of saturation. In this case, the saturation [32] can be defined as $K_6/Q_6$, where $Q_6$ is the reaction quotient for Reaction 6 calculated with equilibrium partial pressures of reactants and products corresponding to the coupling of

TABLE III Calculated partial pressures for coupling of Reactions 2 and 3 at 950 and 850 °C

| Temperature (°C) | Partial pressures (MPa) | | | |
|---|---|---|---|---|
| | $Cl_2$ | $FeCl_3$ | $O_2$ | $TiCl_4$ |
| 950 | $7.5 \times 10^{-2}$ | $2.5 \times 10^{-2}$ | $1.8 \times 10^{-2}$ | $1.4 \times 10^{-5}$ |
| 850 | $8.4 \times 10^{-2}$ | $1.3 \times 10^{-2}$ | $9.3 \times 10^{-3}$ | $7.9 \times 10^{-6}$ |

TABLE IV Calculated reaction quotients, equilibrium constants and saturations for Reaction 6 at 950 and 850 °C

| Temperature (°C) | $Q_4 = 1/K_2K_3$ | $K_6$ | Saturation = $K_6/Q_6$ |
|---|---|---|---|
| 950 | $3.2 \times 10^6$ | $8.3 \times 10^6$ | 2.6 |
| 850 | $1.7 \times 10^8$ | $4.3 \times 10^8$ | 2.5 |

Reactions 2 and 3, and $K_6$ is the equilibrium constant of Reaction 6. Effective PSB formation requires a saturation greater than unity. It can be easily demonstrated that $Q_6 = (1/K_2K_3)$. Therefore, saturation will be given by $K_2K_3K_6$. Table IV contains the calculated values of saturation at 850 and 950 °C, which are in agreement with the fact that formation of PSB at both temperatures is observed. However, the system behaviour for each oxide disposition was different. For the mixed oxides disposition, more and smaller PSB crystals were formed than for the separated disposition. Moreover, at 950 °C for the mixed oxides disposition and for heating of 1 h and over, starting oxides were not detected by XRD. This suggests that in 1 h the equilibrium conditions have been met. This was not observed for the separated disposition at any temperature or heating time. This can be explained by taking into account that for samples with mixed disposition, in addition to the gaseous–solid reaction, the solid–solid reaction could be a contribution to PSB formation, at least in the nucleation step. Then it is possible that the number of nuclei was greater in the case of mixed disposition. If so, for a given saturation (greater unity) and for the same total amount of materials supplied, the overall rate of PSB formation from a greater amount of nuclei will be greater.

## 5. Conclusion

In the present work, pseudobrookite synthesis was performed from $Fe_2O_3$(s)–$TiO_2$(s) powder mixtures in air, argon and chlorine atmospheres at 850 and 950 °C. Two different main pseudobrookite formation mechanisms were observed depending on reaction atmosphere. This can be represented by the following scheme

$$\begin{array}{ccc} Fe_2O_3(s) + TiO_2(s) & = & Fe_2TiO_5(s) \\ + & & + \\ 5\,Cl_2(g) & & 5\,Cl_2(g) \\ \backslash\backslash & & // \\ 2FeCl_3(g) & + TiCl_4(g) & + 5/2O_2(g) \end{array} \quad (12)$$

In air and argon, reaction occurs by means of a solid–solid mechanism in which $Ti^{4+}$ diffuses on the $Fe_2O_3$(s) surface and forms a pseudobrookite layer around $Fe_2O_3$(s) particles and then the progress of the reaction is controlled by solid-state diffusion through this layer. In chlorine, an alternative route of PSB formation by vapour mass transport through gaseous chlorides was observed. The partial pressures of gases at working temperatures give the appropriate saturation which allows the formation and growth of PSB faceted crystals.

## References

1. S. AKIMOTO, T. NAGATA and T. KATSURA, *Nature* **179** (1957) 37.
2. L. PAULING, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **73** (1930) 97.
3. R. W. G. WYCKOFF, "Crystal structures", Vol. 3 (Wiley, New York, 1964).
4. J. F. W. BOWLES, *Am. Mineral.* **73** (1988) 1377.
5. D. RUMBLE III (ed.), in "Oxide minerals", Vol. 3, Ch. 2 (Mineralogical Society of America, Washington, DC, 1981) pp. L61–L79.
6. M. D. KARKHANAVALA and A. C. MOMIN, *J. Am. Ceram. Soc.* **42** (1959) 399.
7. J. B. MAC CHESNEY and A. MUAN, *Am. Mineral.* **44** (1959) 926.
8. A. H. WEBSTER and N. F. H. BRIGHT, *J. Am. Ceram. Soc.* **44** (1961) 110.
9. R. W. TAYLOR, *Am. Mineral.* **49** (1964) 1016.
10. R. R. MERRIT and A. G. TURNBULL, *J. Solid State Chem.* **10** (1974) 252.
11. A. NAVROTSKY, *Am. Mineral.* **60** (1975) 249.
12. I. E. GREY and R. R. MERRIT, *J. Solid State Chem.* **37** (1981) 284.
13. G. BAYER, *J. Less Common Metals* **24** (1971) 129.
14. J. J. CLEVELAND and R. C. BRADT, *J. Am. Ceram. Soc.* **61** (1978) 478.
15. N. H. J. GANGAS, J. KALRADIS, A. MOUKARIKA, A. SIMOPOULOS, A. KOSTIKAS and V. PAPAEFTHIMIOU, *J. Phys. C Solid State Phys.* **13** (1980) L 357.
16. J. M. R. CRUZ, P. C. MORAIS and K. SKEFF NETO, *Phys. Lett. A* **116** (1986) 45.
17. U. ATZMONY, E. GUREWITZ, M. MELAMUD and H. PINTO, *Phys. Rev. Lett.* **43** (1979) 782.
18. S. E. HAGGERTY and D. H. LINDSLEY, *Carnegie Inst. Wash. Year Book* **68** (1970) 247.
19. M. D. KARKHANAVALA and C. M. MOMIN, *Econ. Geol.* **54** (1959) 1095.
20. D. BHOGESWARA RAO and M. RIGAUD, *High Temp. Sci.* **6** (1974) 323.
21. I. E. GREY and A. F. REID, *J. Solid State Chem.* **4** (1972) 186.
22. S. K. GUPTA, V. RAJAKUMAR and P. GRIEVESON, *Metall. Trans.* **22 B** (1991) 711.
23. J. ANDRADE GAMBOA and D. M. PASQUEVICH, *J. Am. Ceram. Soc.* **75** (1992) 2934.
24. F. C. GENNARI and D. M. PASQUEVICH, *J. Mater. Sci.* **33** (1998) 1571.
25. H. SCHMALZRIED, "Chemical kinetics of solids" (Weinheim, VCH, New York, 1995).
26. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, "Introduction to ceramics", 2nd Edn (Wiley, New York, 1976).
27. J. F. MARUCCO, J. GAUTRON and P. LEMASSON, *J. Phys. Chem. Solids* **42** (1981) 363.
28. A. MUAN and E. F. OSBORN, "Phase equilibria among oxides in steelmaking" (Addison-Wesley, MA, 1965).
29. D. R. LIDE Jr (ed.), in "JANAF thermochemical tables", Vol. 14 (National Bureau of Standards, New York, 1985).
30. F. C. GENNARI and D. M. PASQUEVICH, *J. Mater. Sci. Lett.* **15** (1996) 1847.
31. E. M. LOPASSO, J. J. ANDRADE GAMBOA, J. M. ASTIGUETA and D. M. PASQUEVICH, *J. Mater. Sci.* **32** (1997) 3299.
32. B. R. PAMPLIN (ed.), in "International series on the science of the solid state", Vol. 16, in "Crystal growth", 2nd Edn (Pergamon Press, Oxford, 1980) p. 23.

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