

The composition of magnesium titanates as a function of the synthesis method

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Abstract

This paper demonstrates that the composition of the magnesium titanates obtained by precipitation with NaOH from $\text{Ti}^{4+}/\text{Mg}^{2+}$ acid solutions, depends on the molar ratio $\text{Ti}^{4+}/\text{Mg}^{2+}$, the synthesis procedure and the pH of precipitation.

INTRODUCTION

The synthesis of magnesium titanates by coprecipitation of $\text{Ti}^{4+}/\text{Mg}^{2+}$ solution in different molar ratios has been studied by Popkovich and Sviridov [1] and Baura-Peña and co-workers [2–4].

The results of these authors do not always coincide, although in all cases the titanium:magnesium molar ratio of the precipitates were the same as in the respective initial solutions, which indicated that the precipitation was always quantitative, see Table 1.

In the present study, it is deduced that the composition of the precipitates depends on the synthesis method.

EXPERIMENTAL

Materials

Titanium (fine powder form), $\text{MgSO}_2 \cdot 7\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, H_2SO_4 (95–97%), HCl solution (37%) and NaOH, all from Merck, (AnalaR quality) were used.

Preparation of the sample

A sulphuric solution of Ti^{4+} was prepared as described in ref. 2. The hydrochloric solution was prepared as follows: NaOH was added to the sulphuric solution of Ti^{4+} , and the precipitate obtained was filtered,

TABLE 1
X-ray powder diffraction data

T (°C)	Mg ²⁺ /Ti ⁴⁺ 1/1 M		Mg ²⁺ /Ti ⁴⁺ 2/1 M		Mg ²⁺ /Ti ⁴⁺ 1/2 M	
	Ref. 1	Ref. 2	Ref. 1	Ref. 3	Ref. 1	Ref. 4
500	MgTiO ₃	Amorphous	MgTiO ₃ + MgO		MgTi ₂ O ₅	Amorphous
700	MgTiO ₃	MgTiO ₃	MgTiO ₃ + MgO	Mg ₂ TiO ₄ + MgTiO ₃ + MgO	MgTi ₂ O ₅	MgTi ₂ O ₅
900	MgTiO ₃	MgTiO ₃	MgTiO ₃ + MgO	Mg ₂ TiO ₄ + MgTiO ₃ + MgO	MgTi ₂ O ₅	MgTi ₂ O ₅
1000	MgTiO ₃	MgTiO ₃	MgTiO ₃ + MgO + Mg ₂ TiO ₄	MgTiO ₃ + MgO	MgTi ₂ O ₅	MgTi ₂ O ₅
1200	MgTiO ₃	-	Mg ₂ TiO ₄ + MgTiO ₃ + MgO (traces)	-	MgTi ₂ O ₅	-
1300	-	-	-	Mg ₂ TiO ₄	-	-

washed with cold distilled water, and dissolved in a concentrated solution of hydrochloric acid.

The required amount of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was added to the acid solutions of Ti^{4+} to give solutions with $\text{Ti}^{4+}/\text{Mg}^{2+}$ ratios of 1/1 M.

Precipitates were obtained by adding a concentrated aqueous solution of sodium hydroxide, drop by drop, to the sulphuric or hydrochloric solution of titanium and magnesium, until pH 8 was reached. The gelatinous, white precipitates obtained were filtered, washed and dried at room temperature.

The filtrates were analysed for titanium content by spectrophotometry with 2% chromotropic acid, and for magnesium content by complexometric titration with ethylenediaminetetraacetic acid (EDTA). The analysis was negative for titanium and positive for magnesium indicating that the precipitation of magnesium was not quantitative.

According to ref. 2, when the precipitation was carried out from $\text{Ti}^{4+} + \text{Mg}^{2+}$ mixed acid solutions, the total precipitation of magnesium is necessary to reach a pH value above 11.

The results from the thermal analysis and the X-ray powder diffraction of the precipitates obtained from hydrochloric and sulphuric solutions were similar; therefore, only the latter is described.

Apparatus

Thermogravimetric (TG) analysis

A Mettler TA 3000 system with TG50 attachment was used at a heating rate of 600°C h^{-1} .

Differential thermal analysis (DTA)

A laboratory-constructed system incorporating a vertical furnace and a temperature regulation system, both from Adamel, and a differential chromel–alumel thermocouple were used. The heating rate was 300°C h^{-1} .

X-ray powder diffraction

A Philips PW 1130 diffractometer was used, with a Ni filter and $\text{Cu K}\alpha_1$ radiation.

RESULTS AND DISCUSSION

The results of the differential thermal analysis (DTA) of the precipitate obtained in this study are shown in Fig. 1 and Table 2, together with the results of Popkovich and Sviridov [1] and Baura-Peña et al. [2]. The three precipitates described were obtained from $\text{Ti}^{4+}/\text{Mg}^{2+}$ 1/1 M solutions.

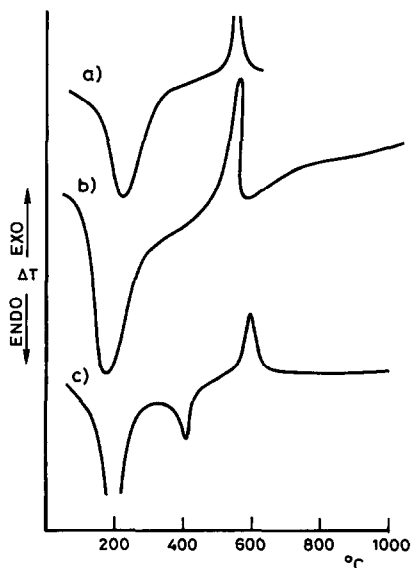


Fig. 1. DTA curves. (a) Curve obtained in this study; (b) curve obtained by Popkovich and Sviridov [1]; (c) curve obtained by Baura-Peña et al. [2].

The three DTA curves show an endothermic peak, caused by loss of the water of hydration, and an exothermic peak. But only the DTA (Fig. 1, curve c) displays an endothermic peak due to the dehydroxylation.

The thermal behaviour of the precipitate obtained by us at pH 8 (Fig. 1, curve a) was similar to that of the precipitate obtained by Popkovich and Sviridov [1] (Fig. 1, curve b), although the former was obtained from an acid solution added to a solution of sodium hydroxide until pH 8, and the latter was precipitated by adding the Ti^{4+}/Mg^{2+} 1/1 M acid solution to the solution of sodium hydroxide; when the precipitation was complete, the pH was approximately 8 [1]. Because of the different methods of preparation of the precipitates, the precipitation of titanium and magnesium was total in the latter case as the precipitation took place in an interval of alkaline pH. In contrast for the former case, the majority of the precipitate

TABLE 2

Peak temperatures of DTA curves of Fig. 1

Curve	1st endo peak (°C)	2nd endo peak (°C)	Exo peak (°C)
(a)	215	—	575
(b)	160	—	563
(c)	185	380	595

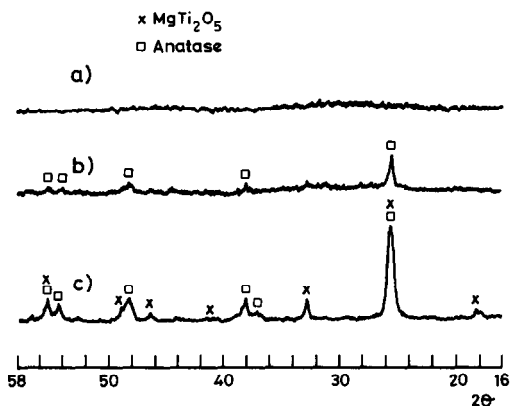


Fig. 2. X-ray diffraction patterns of the precipitate obtained in this study. (a) At room temperature; (b) at 400 °C; (c) at 650 °C.

was formed in an interval of acid pH and the precipitate was deficient in magnesium.

The X-ray diffraction pattern of the precipitate obtained in the present study (Fig. 2, curve a) indicates that the precipitate was amorphous. This result agrees with that given by Popkovich and Sviridov [1].

The X-ray diagrams of the samples taken at predetermined points on the DTA curve of the precipitate obtained in this paper (Fig. 1, curve a) are shown in Fig. 2.

The X-ray diagram (Fig. 2, curve b) of the sample taken at 400 °C, after completion of dehydration, indicates the presence of anatase, TiO_2 ; this agrees with the result obtained by Baura-Peña et al. in the study of the precipitation from sulphuric solutions of titanium [5]. In contrast, the precipitate obtained by Popkovich and Sviridov [1] at 400 °C was amorphous.

The X-ray diagram (Fig. 2, curve c) of the sample taken at the end of the exothermic peak (650 °C), corresponded to a mixture of karrooite, MgTi_2O_5 , and anatase, the latter being the major component. In the study of Popkovich and Sviridov [1], the X-ray diffraction pattern of the sample taken at the end of the exothermic peak indicated only geikielite, MgTiO_3 .

A comparison of the X-ray diagrams in Fig. 2, curves b and c reveals that anatase crystallises better when the temperature of calcination is higher. This result agrees with that given by Baura-Peña et al. [5].

The exothermic peak of Fig. 1, curve a corresponds to the formation of karrooite: this exothermic peak is identical to that given by Baura-Peña et al. [4].

It is known that the quantitative precipitation from solutions of Ti^{4+} by alkalis takes place even at acid pH. The precipitation begins at pH 1 [5,6], so that at pH 8 (the pH of precipitation used in this paper) the majority of

TABLE 3

Precipitation at pH 8

Precipitate	pH change	Solid phases	
		400 °C	650 °
This work	0 → 8	TiO ₂	TiO ₂ + MgTi ₂ O ₅
Popkovich and Sviridov	14 → 8	Amorphous	MgTiO ₃

the titanium precipitated as TiO₂·nH₂O. Moreover, a strongly alkaline medium is necessary in order that all the magnesium is precipitated as Mg(OH)₂ [7].

Therefore, the karrooite found in the X-ray diagram (Fig. 2, curve c) was formed from a small amount of Mg²⁺ precipitated together with the last amount of Ti⁴⁺. As Mg(OH)₂ is not formed, the dehydroxylation peak is not present in the DTA curve (Fig. 1, curve a). Nor is the dehydroxylation peak present in the DTA curve (Fig. 1, curve b), although the precipitation of Mg²⁺ was quantitative: this was due to the synthesis procedure.

Table 3 shows the results of the precipitation at pH 8.

Finally, the DTA curve (Fig. 1, curve c) corresponds to the precipitate obtained from the acid solution of Ti⁴⁺/Mg²⁺ 1/1 M by adding aqueous sodium hydroxide until pH 12 was reached. By progressive calcination, geikielite was obtained at 650 °C, which indicated that the precipitation of magnesium was quantitative.

The dehydroxylation peak at 380 °C indicates that the magnesium that was not precipitated with the titanium precipitated as Mg(OH)₂ in the pH interval 8–12.

In conclusion, the results of this paper indicate the influence of the method of synthesis of magnesium titanates on their composition.

REFERENCES

- 1 G. Popkovich and V. Sviridov, Zh. Neorg. Khim., 20(12) (1975) 3183.
- 2 M.P. Baura-Peña, M.J. Martínez-Lope and M.E. García-Clavel, J. Mater. Sci., 26 (16) (1991) 4341.
- 3 M.J. Martínez-Lope, M.P. Baura-Peña and M.E. García-Clavel, Thermochim. Acta, (1992) in press.
- 4 M.P. Baura-Peña, M.J. Martínez-Lope and M.E. García-Clavel, J. Am. Ceram. Soc., (1991) in press.
- 5 M.P. Baura-Peña, M.J. Martínez-Lope and M.E. García-Clavel, Thermochim. Acta, 179 (1991) 89.
- 6 C. Duval, Inorganic, Thermogravimetric Analysis, 2nd edn., Elsevier, Amsterdam, 1963, p. 289.
- 7 C. Duval, Inorganic Thermogravimetric Analysis, 2nd edn., Elsevier, Amsterdam, 1963, p. 214.