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A STUDY OF THE THERMAL DECOMPOSITION OF c-$Fe_2P_4O_{12}$

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The conditions of preparation of diferrous cyclo-tetraphosphate (tetrametaphosphate) have been followed by thermal decomposition (dehydration) of the phosphorus compound obtained from a mixture of iron and phosphoric acid. The methods of non-isothermal TA and analysis of the calcinates prepared under the same conditions in an electric furnace have been used to determine the temperatures of the individual dehydration and condensation reactions, the temperature regions of the existence of intermediates, and the conversion degree of the calcinate into the final product. It has been shown that the reactions are affected in a distinctly favourable way by increased water vapour pressure in the area of the products being formed.

No case of investigation of the formation of c-$Fe_2P_4O_{12}$ by TA is given in the literature. Only reports [1, 2] describe the formation of this compound during the calcination of a mixture of iron powder and phosphoric acid or diferrous dihydrogenphosphate dihydrate, no details of the temperature and reaction conditions being given except for the statement that the reaction necessitates an inert atmosphere or vacuum. In the presence of air, iron is allegedly oxidized to the Fe(III) state, which results in the partial or complete formation of the condensation product containing the linear phosphate anion instead of the cyclic one. The physico-chemical properties of the product [1] are then quite different and do not meet the requirements put forward in our laboratory, i.e. those of an anticorrosive thermostable pigment [3] or a long-acting microelement fertilizer.

Experimental

The starting compound was prepared by carefully mixing (under Kipp's conditions) 1 mol iron powder with 2.01 mol at the temperatures by 70–90° higher. In this case it is already obvious that the water vapour pressure affects not only the temperature and the rate of the process but also the mechanism and yield of the reactions (Fig. 2). At lower pressures an undesirable splitting off of a part of the phosphorus component in the form of phosphoric or diphosphoric acid takes place

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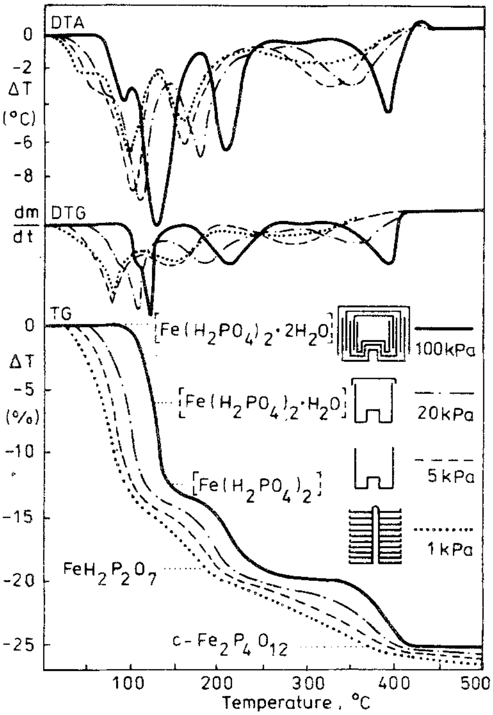

Fig. 1 Thermal curves of starting phosphate

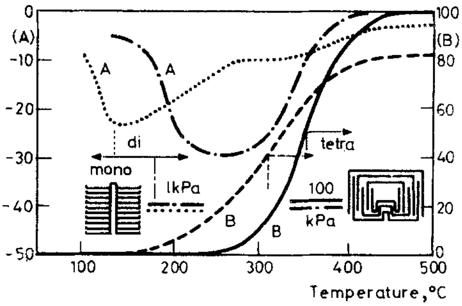

Fig. 2 Extraction experiments (A) – Δm, % (butanon); (B) – degree of conversion to the c-$Fe_2P_4O_{12}$

which then condensates separately to higher polyphosphoric acids, and the yield of the main condensation product is lowered. The increased content of the Fe(II) component able of further reaction is then compensated by the formation of undesirable $Fe_2P_2O_7$. This result was confirmed by both IMA (instrumental analytical methods) and extraction experiments: the butanone-extractable portions from the calcinate obtained in the etage within the temperature interval of the first condensation reactions were found to be lower which indicates a lowered phosphoric acid (concentration of 50% H_3PO_4). Within several days the mixture completely reacted, solidified, and the IMA methods confirmed [2, 4] that it practically corresponded to Fe(II) dihydrogenphosphate dihydrate. The thermal analyses of the phosphate under dynamic non-isothermal conditions were carried out with a derivatograph Q–1500, at first under argon and then in air atmospheres. A slow temperature increase of 1.25 deg/min was used, the sample carriers being in the form of four platinum crucibles (Fig. 1) enabeling the water vapour released from the phosphate to be retained at various pressures [5]. The calcinate samples for analyses were then prepared in an electric furnace, the temperature increase and sample carriers being the same as in the TA. The samples were analyzed with thin-layer chromatography [6], IR-spectroscopy [2], X-ray diffraction analysis [7], and, after dissolution by boiling with hydrochloric acid, also with AAS method. The temperature regions of existence of the individual condensation products and intermediates and the conversion degree to the cyclo-tetraphosphate were also determined by an extraction methods developed in our laboratory, i.e. by the extraction with butanone [8] and with 0.3 M HCl [9].

Results and discussion

The temperatures of the individual processes of the thermal decomposition (dehydration) of the starting phosphate were determined by TA under argon (Fig. 1). The water release corresponding to two water molecules (crystal water) takes place in an endothermic process depending on the type of the crucible used, i.e. on the water vapour pressure in the sample area: the beginning at 40, 50, 60, 100° (at 1, 5, 20, 100 kPa, resp.) and the end at a temperature by 50–60° higher. The corresponding DTG and DTA curves are distinctly divided into two parts (i.e. one for each H_2O molecule). The next water molecule (the constitutional water, this time) is released again in an endothermic process accompanied by the condensation of phosphate anion into dihydrogen diphosphate, the beginning being respectively at 100, 110, 130 and 180° for the individual crucibles. The process is over amount of the desirable intermediate-dihydrogen diphosphate in the calcinate [8]. The splitting off of the second constitutional water molecule in the next endothermic process connected with the second condensation reaction (formation of c-$Fe_2P_4O_{12}$) takes place within a relatively broad interval under the TA conditions, the limits being again shifted according to the actual water vapour pressure in the sample area: 200–375°, 210–390°, 220–400°, and 250 (and/or 360)–410° at 1, 5, 20, and 100 kPa, respectively. At lower pressures the sample weight continues to decrease slowly, which is due to the above-mentioned side condensation reactions of the split off phosphorus component to polyphosphoric acids continuing at higher temperatures, too. Thereby the product yields are decreased by as much as a quarter (Fig. 2). The mild exothermic effects observed in the DTA curves after completed formation of c-$Fe_2P_4O_{12}$ correspond to crystallization of this initially amorphous product.

The TA in air showed that no undesirable oxidation of the Fe(II) component took place at sufficient water vapour pressure (the labyrinth crucible), hence it is not necessary to work with inert atmosphere or in vacuum [1, 2]. This is the second significant result, which is of technological meaning too.

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Zusammenfassung — Die Bedingungen für die Darstellung verschiedener Zyclotetraphosphate (Tetrametaphosphate) durch thermische Zersetzung (Dehydratierung) einer aus einem Gemisch von Eisen mit Phosphorsäure gewonnenen Phosphorverbindung wurden untersucht. Zur Bestimmung der Temperaturen der einzelnen Dehydratierungs- und Kondensationsreaktionen, der Temperaturbereiche für die Existenz von Zwischenprodukten sowie des Konvertierungsgrades der Kalzinate zu den Endprodukten wurden nicht-isotherme TA-Methoden und auch eine Untersuchung der unter gleichen Bedingungen in einem elektrischen Brenner gefertigten Kalzinate angewendet. Es wurde gezeigt, daß die Reaktion auf eindeutig bevorzugte Weise durch erhöhten Wasserdampfdruck über den zu fertigsenden Produkten beeinflußt wird.

Резюме — Условия получения диферроциклотетрафосфата (тетраметафосфата) были изучены путем термического разложения (дегидратации) фосфорсодержащего соединения, полученного из смеси железа и фосфорной кислоты. Метод неизотермического ТА и анализ продуктов, полученных при прокаливании этого соединения в электрической печи, были использованы для определения температур отдельных реакций дегидратации и конденсации, температурных интервалов существования промежуточных продуктов и степень превращения продуктов обжига до конечных продуктов реакции. Показано, что реакции отчетливо затрагиваются путем увеличения давления паров воды в зоне образующихся продуктов.