THEORETICAL AND EXPERIMENTAL RESULTS FOR THERMAL PHOSPHATE DISSOCIATION IN PLASMA

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ABSTRACT

The 100 kW plasma heating device is used to study thermal phosphorite dissociation in the air plasma flow. As a result of the cooling of the dissolved substances, both phosphor oxides and condensed containing-calcium phosphates can be produced as end products. The thermodynamics of the dissociation process is investigated.

1. INTRODUCTION

The phosphate ore is at present processed primarily by acids (when mineral acids are used for ore decomposition) and electrothermally (when the ore is reduced with carbon in electrothermal furnaces). Because of certain demands for the raw material, these methods are inapplicable for the processing of many phosphor-containing ores, whore resources are limited.In addition, in the electrothermal method phosphor is to be reduced with a great amount of coal, being valuable raw material and then this phosphor is mainly burnt and again converted to the oxidized form. Phosphor oxides are exhausted from phosphates by calcination, but no desirable results are obtained for standard pressure since natural phosphate dissociation temperature could not be attained in thermal furnaces. The development of plasma heating devices made it possible to use phosphate ore dissociation in chemical technology [1].

2. THERMODYNAMICS

Natural phosphate dissociation is a strongly endothermal process. The thermodynamic analysis of the Ca-P-O and Ca-P-O-N systems is made to determine the parameters characterizing the dissociation process since the phosphor-containing part of natural phosphates can be, to some extent, replaced by tricalcium phosphate. The equilibrium assumptions indicate that tricalcium phosphate decomposes at a pressure of 10^5 Pa and at temperatures above 3200 K with subsequent manufacture of gaseous products and condensed calcium oxides (Fig. 1).

The energy consumptions are the primary technical and economic criterion for producing phosphor-containing products. Due to the equilibrium considerations, the minimum energy required for tricalcium phosphate decomposition at 3200 K amounts to 2.30 kcal/mol or 2.68 kWh/kg. As the arc heater energy is spent for the heating of plasma forming and transporting air and ore, the total energy consumptions for this process are higher and affected by the weight phosphate-air ratio and temperature (Fig. 2). Comparison of the air enthalpy at different temperatures and air-tricalcium phosphate enthalpies predicts air plasma temperatures that provide equilibrium tricalcium phosphate dissociation (Fig. 3).

If phosphorite dissociation products are not separated, then according to the thermodynamics, with cooling of a high-temperature phosphor and calcium oxides-containing flow at 10^5 Pa and 3200-2200 K, tricalcium phosphate should be formed irrespective of the $CaO:P_2O_5$ ration; pyrophosphate should be produced at 2200-1500 K with the $CaO:P_2O_5$ ratio equal to two and metaphosphate should be formed at temperatures below 1500 if the $CaO:P_2O_5$ ratio is close to unity.

3. EXPERIMENTAL

Experiments are conducted in the multi-jet plasma reactor with the channel diameter equal to 50 mm [2]. In different runs the processed phosphorite is composed of particles no more than 250 μm with different chemical compositions containing 21-29 % P_2O_5 . The silica - phosphorite mixture (up to 30 %) is also processed. The initial reactor cross section power amounts to 29-82 kW, and the initial mean bulk air-plasma temperature is 3500-6300 K. Experiments are performed on two devices with different thermal insulation of the reactor walls. The reactor efficiency calculated in terms of the initial reactor cross section power and heat losses to the reactor walls varies from 47 to 75 %.

The conversion degree, K_p, [2] is the main parameter served to determine the process efficiency and characterizes phosphor oxide exhaust from the phosphate ore. The quantity K_p is determined with allowance for not only volatile components but also for calcium oxide entrained by the gas flow from the ore. The value of K_p is not affected by a small variation in the chemical composition of the ore as well as by silica additions. The quantity K_p is most substantially affected by the energy consumptions defined as the relation of the initial reactor cross section power to the phosphate mass flow rate (Fig. 4). This quantity also depends on the reactor efficiency and is higher at larger efficiencies.

The analysis of the end products gives that condensed particles, no more than 10 μm in size, are formed alongside with gaseous phosphor oxides. The chemical, γ-phase analysis, IR--spectroscopic studies and paper chromotography suggest that the condensed products are primarily composed of calcium phosphates such as pyrophosphate, tricalcium phosphate, different--polymerization poly-and metaphosphates containing P_2O_5 up to 50 %. The chemical composition of condensed products varies depending on phosphorite processing as well as on product cooling. The condensed phosphates satisfy the requirements for slow-acting fertilizers.

In our experiments the nitrogen oxide content in the gas phase is ~ 4%.

4. REFERENCES

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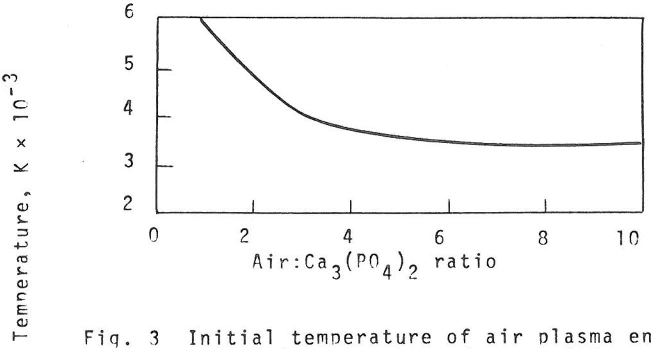

Fig. 3 Initial temperature of air plasma ensuring tricalcium phosphate decomposition versus air-tricalcium phosphate ratio. Pressure is 10^5 Pa.

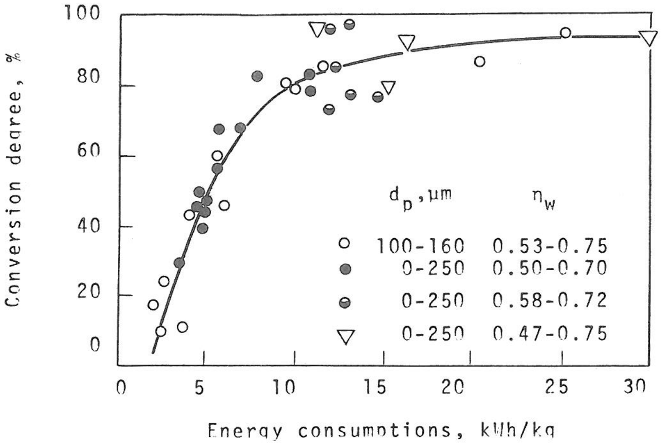

Fig. 4 Experimental phosphate ore conversion degree versus energy consumptions.

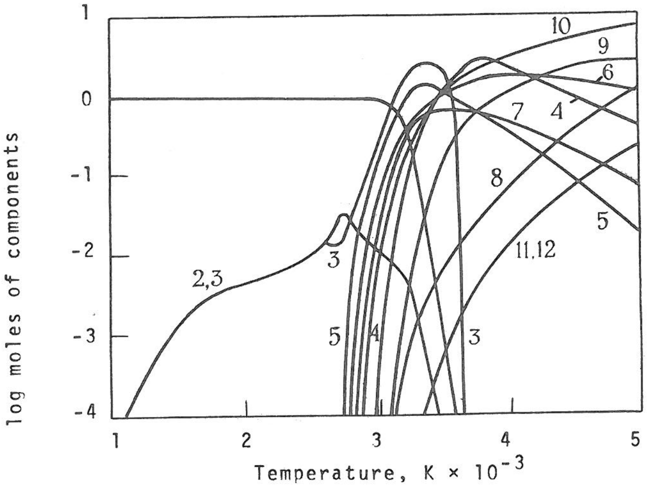

Fig. 1 Temperature dependence of Ca-P-O system composition with 1 mol of tricalcium phosphate at a pressure of 10^5 Pa :1, $Ca_3(PO_4)_2$;2, $Ca_2P_2O_7$; 3, condensed CaO; 4, gaseous CaO;5, PO_2; 6,PO; 7, O_2; 8,P; 9,Ca;10, O;11,Ca^+;12, electrons.

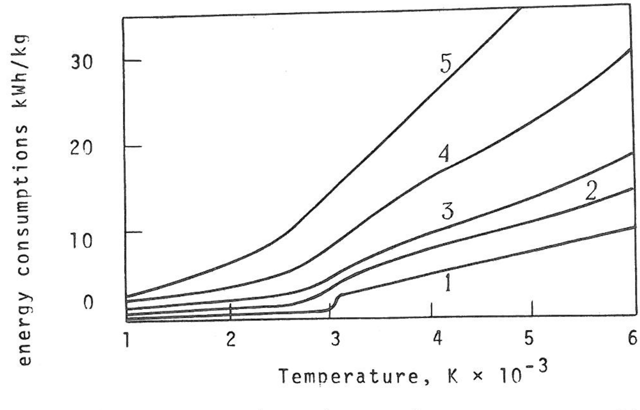

Fig. 2 Temperature dependence of energy consumptions for heating and dissociation of 1 kg of tricalcium phosphate at weight $Ca_3(PO_4)_2$:air ratios: 1,1:0;2,1:1;3,1:2; 4, 1:5; 5, 1:10. $p=10^5$ Pa.