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Review

Phase transformation of glass-ceramics produced by naturally cooled yellow phosphorus slag during calcination

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A B S T R A C T

Naturally cooled phosphorus slag is formed during the production of phosphorus, which contributes to a serious environmental pollution. The crystallization kinetics has already been evaluated in previously published studies during the process of $CaO-Al_2O_3-SiO_2$(CAS) glass-ceramics preparation from naturally cooling phosphorus slag. This study was focused on calculating the thermodynamic equilibrium phases of Ca, Al and Si using FactSage6.4 thermodynamic software package at different temperatures. X-ray diffraction, Fourier transform infrared spectroscopy and Scanning electron microscopy were employed to examine the phase status of Ca, Al and Si elements. The results showed that phase transformation started at 450 °C and formation of liquid slag phase occurred at 950 °C in naturally cooled yellow phosphorus slag heated to molten state. The calcium-containing phase had changed to CaO(slag) and $Ca_3(PO_4)_2$ at high temperatures. Also, aluminum-containing components present in liquid Al_2O_3 slag phase formed at 1000 °C and silica-containing phase at high temperatures were dominated by SiO_2, $CaSiO_3$, and SiO_2(-slag). Finally, SiO_2 and further migration to molten SiO_2(slag) were noticed as the temperature rose.

Contents

1. Introduction

Yellow phosphorus slag is formed during process of yellow phosphorus manufacturing from phosphate rock, cock, and silica [1]. Naturally cooled yellow phosphorus is formed during high temperature molten slag generated during the production of

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yellow phosphorus placed in air or other media at slow cooling rates. It is estimated that 8-10t yellow phosphorus slag is generated from the production of 1t of phosphorus [2,3]. The yellow phosphorus slag does not only pollute the environment but also occupies large spaces. Yellow phosphorus slag contains CaO and SiO_2 and the slag is made of Al_2O_3, TiO_2, Fe_2O_3, P_2O_5, MgO, F, K_2O and Na_2O, among others. Therefore, full utilization of phosphorus slag could have great social value and economic benefits. Consequently, conversion of yellow phosphorus slag into more valuable and environmentally friendly materials is important for development and environmental protection. The utilization of phosphorus slag was widely studied, especially in China, for the preparation of agricultural calcium fertilizer [4], ceramic material [5], silica [6], glass material [7], and glass-ceramics [8]. In particular, the application of phosphorus slag in high value-added glass-ceramics is an effective way to make a comprehensive utilization.

Glass-ceramics are fine-grained polycrystalline material synthesized by controlling the composition [9] and heat-treatment [10]. They are characterized by low-cost, low water absorption, high acid resistance, and high mechanical properties. Glass-ceramics and yellow phosphorus slag have similar chemical compositions. Thus, yellow phosphorus slag can be utilized for the production of glass-ceramics, depending on the composition of the slag. These processes could be monitored through methods like FactSage chemical thermodynamic software [11,12], which is widely used in metallurgy, materials, chemical and other fields [1,13–15]. Using Factsage software, Bjørn et al. [16] examined the process of manganese ores calcined in air and phase equilibrium in manganese ores at 800 °C, 1000 °C and 1200 °C in different atmospheres. Cheng et al. [17] studied the competition between Xonotlite and Canasite formation during heat treatment, and showed that crystalline Xonotlite appeared at 700 °C after heating for 1 h. Also, they discovered that the main crystalline phase changed to Canasite after heating at 700–850 °C for 1 h. Increasing the holding time and phase of Xonotlite could yield Canasite at 700 °C. Liu et al. [18] discussed several aspects dealing with phase transformation, including multiphase transformation during the process of copper slag calcination, change from Fe_2SiO_4 to Fe_3O_4 and amorphous SiO_2 in the initial copper slag at 800 °C, as well as Fe_2SiO_4 to Fe_3O_4 at 1000 °C. It is revealed that phase of Fe_2SiO_4 and Fe_3O_4 undergo transformation to Fe_3O_4 and α-Fe_2O_3 at temperatures of 850–1050 °C. The calcination temperature had a greater impact on conversion of Fe_3O_4 into α-Fe_2O_3 if compared to prolonged calcination time. However, the grains of α-Fe_2O_3 were more uniform in size with spherical shapes when prolonged calcination time was utilized. The phase transformation and thermochemical reactions often concurrent during the preparation process of the material at high temperature. The slagging characteristics and minerals conversions during the ashing process of coal were used for equilibrium calculations using Factsage™ [19–27]. However, the migration of Ca, Al and Si elements and their transformation during the process of microcrystalline glass are rarely reported. Besides, most of the reported studies have focused on the mineral conversion but naturally cooled yellow phosphorus slag was less examined. In particular, the formulation and process of yellow phosphorus play an important significance in the mechanism of migration and transformation of calcium, aluminum, and silicon.

This study was mainly focused on the phase change of naturally cooled yellow phosphorus slag during the preparation of glass-ceramics calcination process. The study aimed to provide insights into changes in Ca, Al and Si during the sintering process, and to further explore the mechanism of naturally cooled yellow phosphorus furnace slag during calcination.

2. Materials and methods

2.1. Experimental and procedures

The naturally cooled yellow phosphorus slag received from the Yunnan province of China was first ground and sieved to 180 mesh. The slag was then dried at 105 °C for 24 h and its chemical composition was analyzed by X-ray fluorescence (XRF).

As shown in Table 1, the naturally cooled yellow phosphorus slag contained mainly Ca and Si. The glass-ceramics synthesized with naturally cooled yellow phosphorus slag belonged to the CaO–Al_2O_3–SiO_2(CAS) system. An amount of 53.29 g SiO_2 and 4.42 g Al_2O_3 were added to 100 g of naturally cooled yellow phosphorus slag according to Table 2. The raw materials were then mixed for at least 2 h to ensure full homogeneity. The resulting mixture (15 g) was placed in an alumina crucible and heated in an electric furnace for 5 h. The temperature was raised from 450 to 550, 650, 900, 950, 1000 and 1050 °C and then cooled down to room temperature. The crystalline phase was investigated using an X-ray diffractometer (D/max-2200) between 5° and 90° at a step of 0.02 min^{-1} operating at 36 kV and 30 mA using Cu K_α radiation at $\lambda = 1.5418$. The infrared radiation characteristics were examined using an infrared radiation tester (model NICOLET iS10). The morphology was observed by a VEGA3-SBH scanning electron microscope.

2.2. Thermal equilibrium calculation analysis

In this calculation, the preparation temperature of the glass-ceramics was set to up 1350 °C. The key material (phosphorus slag) and the ingredients (Al_2O_3, SiO_2) were fully melted at 1350 °C, and all phases kept their stabilities. During the Ca, Al and Si phase transformation at high temperatures, the following hypothesizes were assumed: i) the heating process of glass-ceramics was prepared at atmospheric pressure and high temperature, ii) the equilibrium vapor products were treated as ideal gases at certain temperatures with the balance to participate in the reaction, and iii) the liquid phase area above the melting phase was considered as a solution at high temperatures. Thus, the glass-ceramic phases and distribution of Ca, Al and Si elements were calculated using Equilib module based on FToxid and Fact53 databases. Prior to simulations, the parameters were set as follows:

Reactants: The glass-ceramics formulations were calculated as the participant reactants, according to Table 2.

Temperature: The T was varied from 50 °C to 1350 °C with a step length of 100 °C.

Pressure: The atmospheric pressure was set to 101325Pa.

SiO_2 (53.29 g) and Al_2O_3 (4.42 g) were added to the raw material when the naturally cooled yellow phosphorus slag was 100 g in the preparation of CaO–Al_2O_3–SiO_2 system glass-ceramics.

3. Results and discussion

3.1. Migration and transformation of Ca, Al and Si during glass-ceramics process produced with naturally cooled phosphorus slag by FactSage

Fig. 1 shows the amount of the produced calcium minerals at

Table 1
Composition of naturally cooled slag received from a chemical phosphorus enterprise in the Yunnan Province.

Element	O	Ca	Si	Al	Mg	P
Content (wt%)	36.21	34.27	14.21	1.53	3.21	1.65
Element	F	Fe	Na	K	S	Others
Content (wt%)	2.93	0.041	0.16	0.31	0.32	5.16