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Kyanite ore processing by carbochlorination

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ABSTRACT

Kyanite, mullite and model kyanite ore carbochlorination processing was investigated in laboratory experiments and thermodynamics' calculations. The extraction of 94% alumina and silica takes place as a result of calcined kyanite carbochlorination at 1300 °C for 90 min at normal pressure. Kyanite processing into $AlCl_3 + SiCl_4$ gas mixture is proposed for high purity alumina, nanodispersed silica and solar-grade silicon production.

1. Introduction

Kyanite, andalusite, and sillimanite are alkali free anhydrous aluminosilicate minerals with the same chemical composition (Al_2SiO_5). To present day kyanite ($Al_2O_3 \cdot SiO_2$) ores are usually beneficiated by gravity and flotation (Bulut and Yurtsever, 2004) and considered predominantly as a raw material for kyanite concentrate production (~450,000 t/y (Tanner, 2013)). In its turn, kyanite concentrate is a raw material for refractory production and ceramic synthesis, after its conversion to mullite. Mullite is an aluminosilicate with a variable alumina to silica ratio. The composition of mullite ranges between 57 and 92 mol% Al_2O_3 (Fischer et al., 1996). In this paper we dealt with 3/2 sinter-mullite ($Al_6Si_2O_{13}$, 71.8 mol% Al_2O_3) as the product of kyanite thermal conversion. When calcined at high temperatures, sillimanite group minerals are converted to mullite and silica. Kyanite has the lowest decomposition temperature among them (Schneider and Majdic, 1979, 1980, 1981).

Kyanite is the most widely distributed mineral in the Earth crust in Russia. The estimated reserve of Russian kyanite ores is 3.68 billion tons of Al_2O_3 (Lepezin, 2004), that exceeds alumina content in Russian bauxites—the most important ores for aluminum industry. The known Russian bauxite reserves are insufficient for the metallurgical alumina production by the Bayer process—the principal industrial technology for bauxite processing. Russia needs to import part of metallurgical alumina for its aluminum industry and to extract alumina from nepheline ores (alumina content ~27%). In this case, for example, to extract 1 t of Al_2O_3 Achinsk Alumina Refinery—one of the first-rate Russian alumina producer, is forced to discharge to the environment about 6.5–6.8 t of solid wastes only (Shepelev et al., 2012). On the other hand, the alumina content in kyanite concentrate exceeds 60%. But up to this day kyanite concentrate processing for the metallurgical alumina production is considered to be unpromising method owing to some points: (1) the current prices of a raw kyanite concentrate are about $300/t (Tanner, 2013), that is much higher than bauxites's ones; (2) modern industrial technologies for bauxites or nepheline ores processing into metallurgical alumina are unsuitable for kyanite treatment.

In this paper it will be shown, that in addition to refractories and ceramics production, it is possible to obtain another products from kyanite concentrate and kyanite ores as well: metallurgical alumina, microsilica or silica fume (silica amorphous form, made by combustion of silicon tetrachloride in a hydrogen–oxygen flame (Sprung and Kropp, 2001; Flörke et al., 2008), or with this sort of methods), and silicon for solar cells (Parfenov and Pashkov, 2008). It is a proven fact that silicon, titanium and aluminum chlorides can be reduced into metallic powders by aluminum subchloride or hydrogen (Parfenov, 2004; Parfenov and Pashkov, 2007, 2008, 2009; Parfenov et al., 2008; Kartayev et al., 2010; Zakirov et al., 2009a, 2009b, 2010; Yasuda et al., 2011). The synthesis of the metallurgical γ-alumina from $AlCl_3$, and microsilica from $SiCl_4$, has been well studied (Gutsch et al., 2002; Flörke et al., 2008). Full production cycle for above products is predominantly limited by the stage of concentrate (or ore) carbochlorination process. Our previous experiments have proved that it takes 10–30 min at T = 1000–1100 °C to convert titaniferous magnetite, bauxite, kaolinite clay and hematite ores into the mixture of volatile chlorides (Mikhalev and Parfenov, 2008). Kyanite as well as other sillimanite-group minerals and mullites proved to be persistent substances for the carbochlorination processing

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at T ≤ 1100 °C (Zakirov and Parfenov, 2007). To intensify kyanite chlorination, we have proposed a very effective, but expensive method—periodical oxidized/reduced reaction at 1000–1100 °C:

$$Al_2SiO_5 + 2AlCl \rightarrow Si + 2/3AlCl_3 + 5/3Al_2O_3 \rightarrow$$
$$5/3Al_2O_3 + Si + 5CO + 7Cl_2 \rightarrow 10/3AlCl_3 + SiCl_4 + 5CO_2.$$

The heart of the method is the high temperature periodical reduction of Al_2SiO_5 by AlCl and following etching Si + Al_2O_3 solid mixture with carbochlorination. Aluminum subchloride synthesis requires metallic aluminum or electrical energy (Parfenov and Pashkov, 2007; Kartayev et al., 2010). Such method can be promising to put into practice two new technologies: pure aluminum and silicon reduction from their chlorides instead of Al_2O_3 and $SiHCl_3$. But now it seems that carbochlorination processing of kyanite at higher temperature is more perspective approach because of no need of aluminum subchloride.

2. Equipment, chemicals, methods and procedure

The chemical composition of raw kyanite concentrate was studied by the X-ray fluorescence (XRF) method with Axios Advanced PANalytical equipment.

The powder X-ray diffraction (XRD) measurements were carried out by using PANalytical X'Pert PRO diffractometer with Co K_a radiation. The quantitative phase analysis was performed using the full-profile Rietveld method (Rietveld, 1969) and the derivative difference minimization technique (Solovyov, 2004). The weight fractions of crystalline phases W_i and amorphous residue W_r were calculated as follows:

$$W_i = \mu S_i M_i V_i N_i^2 / CT, \quad W_r = 1 - \mu W_i$$

where S_i is the refined scale factor of phase i, M_i and V_i are the unit cell mass and volume, N_i is the space group multiplicity, μ is the mass absorption coefficient, C is the diffractometer constant determined from an external standard (corundum) measurement, and T is the scan counting time.

Karabash kyanite concentrate (Ural, Russia) with the impurity oxides, wt.%: TiO_2—0.5, Fe_2O_3—0.29, Na_2O—0.16, K_2O—0.08, CaO—0.06, was used. To exclude sample mass diminution with $FeCl_x$ evaporation and impurity influence on the crystals structure transformation during carbochlorination, kyanite concentrate was preliminary etched by boiling for 30 min with 35 wt.% HCl solution, rinsed with distilled water and dried at 300 °C for 1 h. Samples of mullite concentrate (calcined kyanite) were prepared by calcination of etched kyanite concentrate at 1300 °C for 3 h in air atmosphere.

Kyanite occurs primarily in schists and gneisses, often in association with quartz (kyanite quartzites), with average content of alumina 15–20%. To examine how kyanite can be processed by carbochlorination in the presence of large quantities of silica, model samples of kyanite ore were prepared by mixing of etched kyanite concentrate with powdered fused silica.

The mean particle size of all used powders (kyanite related materials, alumina, silica and coal) was 60 μm.

DSC results were performed with the Netzsch STA Jupiter 449C instrument. Platinum crucibles with perforated lids were used, a sample mass for the experiment was in the range of 45–50 mg. The kinetics of the kyanite to mullite thermal transformation was studied under a dynamic argon atmosphere at T = 200–1450 °C and heating rates at 3–12 °/min. Program package NETZSCH Thermokinetics was used to process the thermo-kinetic data.

Equilibrium calculations of chemical composition were made with the global free energy minimization (FEM) method. The global free energy is given by

$$G_{tot} = \sum_i^N x_i \left(G_i^0 + RT \ln a_i \right)$$

where x_i represents the moles of species i, G_i^0 is the standard partial molar Gibbs free energy of species i, R is the gas constant, T is the temperature, a_i is the activity. The usual problem is to determine the values of x_i for a given set of gram-atoms of constituent elements, and for a given set of N chemical species together with their G_i^0

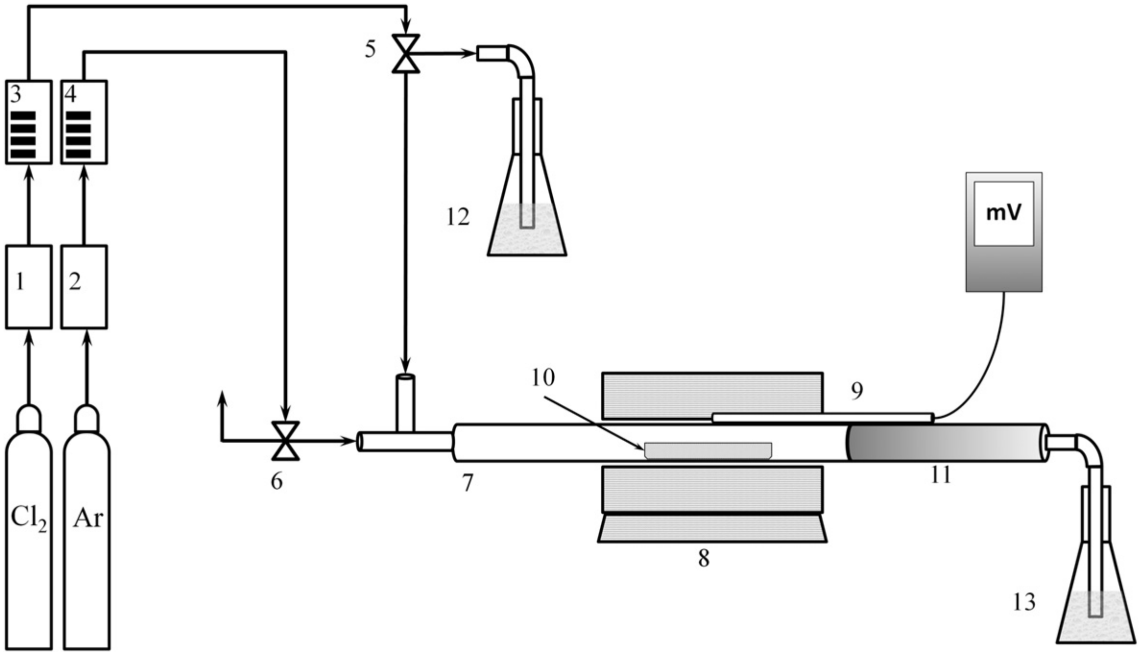

Fig. 1. Layout of laboratory experimental setup for carbochlorination: 1 (H_2SO_4), 2 (silica gel)—dryers; 3, 4—flow-meters; 5, 6—valves; 7—corundum tube; 8—electric tube furnace; 9—thermocouple; 10—porcelain boat with sample; 11—condenser; 12, 13—NaOH solution.