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Synthesis of scheelite with wolframite and calcium carbonate by a direct solid-state synthesis route

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ABSTRACT

Scheelite was successfully prepared by solid-state calcination synthesis using wolframite [$(Fe,Mn)WO_4$] and calcium carbonate as materials in air atmosphere. The effects of processing parameters, such as calcination temperature, holding time and calcium carbonate dosage on conversion ratio of wolframite were investigated. The conversion of wolframite increased with increasing of temperature, holding time and calcium carbonate dosage. The results demonstrated that 97.58% of wolframite was converted to scheelite in 2 h at temperature of 800 °C under the condition of calcium carbonate stoichiometric ratio of 1.3, and the corresponding reaction products are scheelite, iron oxide and manganese dioxide.

1. Introduction

Tungsten minerals that occur in sufficient abundance to be of economic significance are wolframite [$(Fe,Mn)WO_4$] and scheelite ($CaWO_4$) [1,2]. As one of the conventional methods of hydrometallurgical processing scheelite concentrate is a hydrochloric acid based route which was used in the last century [3]. During the digestion reaction, scheelite converted to tungstic acid. The tungstic acid obtained was dissolved in ammonium hydroxide and the solution after purification was crystallized to ammonium paratungstate (APT). At present, wolframite and scheelite were digested in sodium hydroxide or sodium carbonate solution, and raw sodium tungstate solution was obtained [4–8]. Then the sodium tungstate solution was treated by solid ion exchange resins or liquid extractant. In the process, sodium tungstate was converted to ammonium tungstate, and the separation of sodium was also achieved simultaneously [9,10]. In these methods of processing tungsten ores, sodium hydroxide, sodium carbonate and hydrochloric acid were used as leaching reagent. But closed circulation of the leaching solution cannot be achieved, because it is difficult to separate sodium ion and chloride ion from the solution through chemical precipitation method or other methods. So, the above mentioned methods of processing tungsten ores inevitably produced lots of wastewater that contained sodium and chloride ions. China produced about 190,000 tons of APT products annually, resulting in the creation of 24 million tons of wastewater containing Na^+ and Cl^- in the ion exchange process [11]. According to the new regulations of China Ministry of Environmental Protection, wastewater free emission was enforced in tungsten hydrometallurgical processing [11]. Thus, tungsten manufacturers shall meet strict environmental emission standards or be shut down within a short time.

In order to solve the problem of wastewater emission existing in current tungsten hydrometallurgical extraction approach, Jiangxi University of Science and Technology developed a new environmentally friendly technology of processing scheelite, known as "closed circuit hydrometallurgical extraction of tungsten from scheelite in ammonium invariable system" [12]. Wastewater free emission in the process of extracting tungsten from scheelite can be achieved with this technology, which has been successfully put into industrial practice. In the approach, scheelite was digested well with a mixture of $(NH_4)_3PO_4$ and ammonia water in an autoclave (leaching yield 99.1%), and then raw ammonium tungstate solution was obtained directly. However, wolframite cannot be decomposed by the mixture of $(NH_4)_3PO_4$ and ammonia water. So, we attempted to convert wolframite into scheelite, so that green hydrometallurgical processing wolframite can also be achieved. So far, synthesis of scheelite from tungstate solution has been successfully put into practice [13–15], but the method of converting wolframite to scheelite has not been reported yet. Mineralogical studies showed that deposition of primary scheelite is often associated with calcite [16,17]. Inspired by the interesting phenomenon that exists in scheelite geological mineralization process, we developed a new way of synthesizing scheelite using wolframite and calcium carbonate by solid-state

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Table 1
Chemical composition of wolframite (mass fraction, %).

Composition	WO_3	Fe_2O_3	MnO	SiO_2	Al_2O_3	Nb_2O_5	CaO	SO_3	MgO	P_2O_5
Mass fraction%	70.31	8.29	14.84	1.30	1.07	1.36	0.44	0.27	0.07	0.08
Composition	K_2O	CuO	ZnO	As_2O_3	Rb_2O	Y_2O_3	MoO_3	SnO_2	Ta_2O_5	Bi_2O_3
Mass fraction%	0.42	0.06	0.12	0.04	0.02	0.02	0.06	0.81	0.32	0.13

calcination synthesis in air atmosphere. The reaction mechanism for the synthesis of scheelite can be expressed by the following equation:

$$2FeWO_4 + 2CaCO_3 + 1/2O_2 = 2CaWO_4 + Fe_2O_3 + 2CO_2\uparrow \quad (1)$$

$$2MnWO_4 + 2CaCO_3 + 1/2O_2 = 2CaWO_4 + Mn_2O_3 + 2CO_2\uparrow. \quad (2)$$

In this work, various operating conditions were studied in detail in order to select the optimized processing parameters.

2. Experimental

2.1. Materials

The wolframite used in the study was from Ganzhou in Jiangxi Province of China and was ground in a ball grinder. After crushing and grinding, the particle size of the ore was mainly distributed around 0.074 mm. The ore ground was analyzed by chemical method and characterized by X-ray powder diffraction analysis (Philips Model 1010). The wolframite chemical composition was shown as Table 1. X-ray diffraction (XRD) analysis showed that tungsten was mainly in the form of (Fe,Mn)WO_4 (Fig. 1). The calcium carbonate was industrial pure provided by Chengdu Kelong Chemical Reagent Manufactory.

2.2. Equipment and procedure

Synthesis of scheelite experiments were carried out in a muffle furnace under air atmosphere. The temperature was set at the predetermined value. When the temperature rose to the predetermined value, then the desired amount of wolframite and calcium carbonate were added into the furnace at the same time. After a desired time, the calcination product was taken out form the furnace, and then was analyzed by chemical method and characterized by X-ray powder diffraction. The respective mass fraction of wolframite and scheelite in the calcination product cannot accurately analyzed by phase analysis method (XRD). Based on the fact that scheelite can be completely decomposed (leaching yield 99.5%) with a mixture of ammonium phosphate and ammonia water under the conditions of stoichiometric ratio

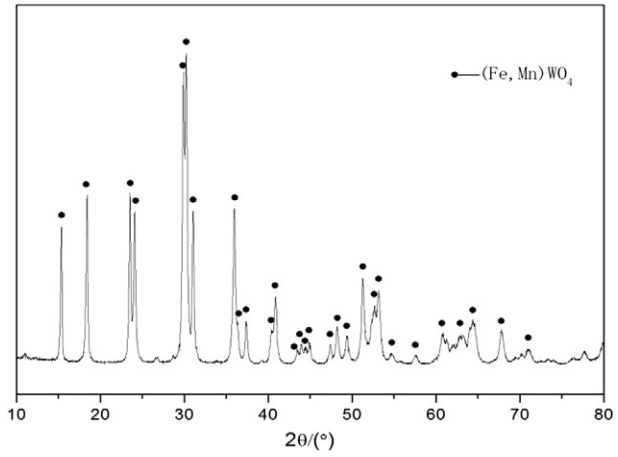

Fig. 1. XRD pattern of wolframite.

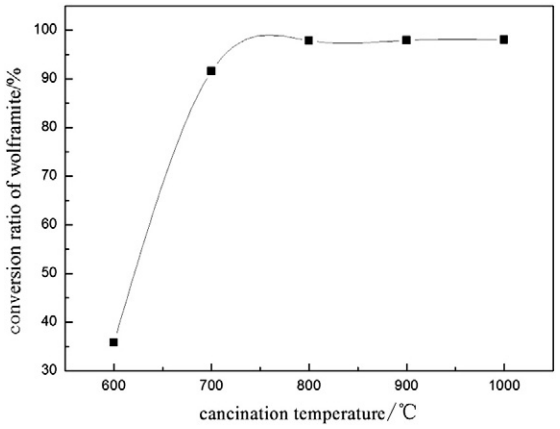

Fig. 3. Effect of calcination temperature on the conversion ratio of wolframite.

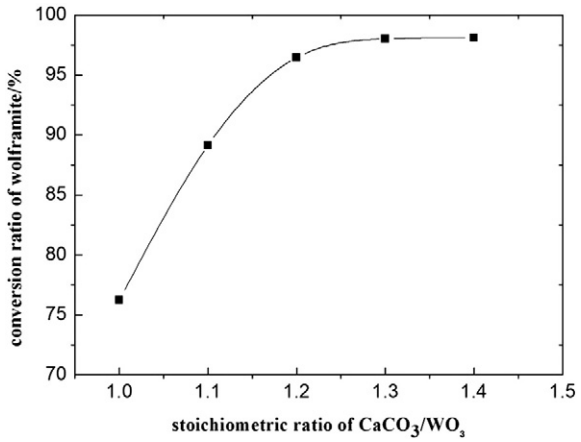

Fig. 2. Effect of dosage of $CaCO_3$ on the conversion ratio of wolframite.

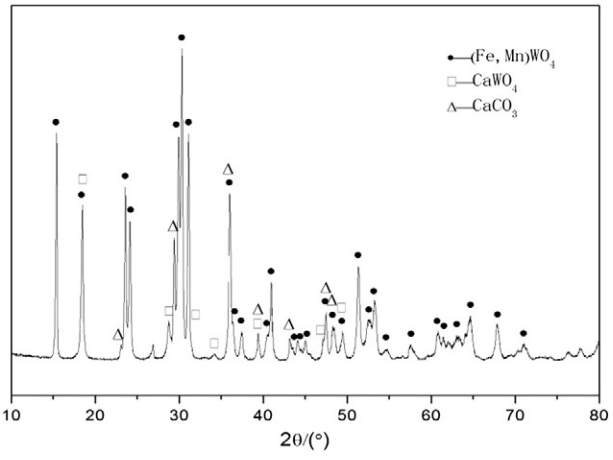

Fig. 4. The XRD pattern of calcined product under temperature 600 °C.