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Effect of rare earth oxides on the properties of bio-soluble alkaline earth silicate fibers

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Abstract: Using natural mineral wollastonite, talc and quartz sands as raw materials, rare earth oxides (La_2O_3, Nd_2O_3 and Y_2O_3) as additives, the bio-soluble alkaline earth silicate fibers were prepared by melting and blowing process. The viscosity of the molten materials, bio-solubility and crystallization behavior of the fiber were investigated. The results indicated that the fiber drawing temperature range could be broadened since the slope of the temperature-viscosity curve decreased with adding rare earth oxide. The addition of rare earth oxide was beneficial to the increase of crystallization temperature by strengthening the network structure of the fiber. The existence of rare earth oxide in the fibers would reduce the solubility of the fibers, which still belonged to bio-soluble fibers.

Keywords: rare earth oxide; alkaline earth silicate fibers; bio-solubility; crystallization behavior

Traditional aluminum-silicate refractory ceramic fibers (RCF) have potential health hazard when they find their way into the lung of human beings[1–3]. In recent years, the new kind of alkaline earth silicate fibers (AES) have been developed, which exhibit high solubility in human body lung fluid[4,5]. The bio-soluble fibers can replace refractory ceramic fibers as insulation materials in some application areas.

Generally, the alkaline earth silicate fiber compositions include CaO-MgO-SiO_2, MgO-SiO_2 or CaO-SiO_2 system and are produced by an electric melting and spinning or blowing process[5], which is the same technology used around the world to manufacture RCF. The viscosity of the silicate melts at fiber formation temperature range is critical for a given fiber composition, and the suitable viscosity value is about 0.5–5 Pa·s. In order to estimate the bio-solubility of the fibers, most of these determinations are usually carried out *in vitro* using physiological saline solutions[6]. In practical application of fiber used as furnace lining, the devitrification of the fiber takes place and as a result becomes more rough, which is mainly caused by the formation of crystalline phases. The growth of crystal causes the destruction and pulverization of the fibers in high temperature application with long exposure time[7].

In this paper, the studies focused on the effects of rare earth oxide additions on melt viscosity, the solubility of the AES fibers in simulated human body fluid, and crystallization behavior of the fibers.

1 Experimental

1.1 Fiber preparation

The samples of alkaline earth silicate fibers were prepared in an electirc induction furnace using a blowing device. Natural mineral wollastonite, talc and quartz sands (purchased from SIYUAN Corporation in China) have been used as the main raw materials and rare earth oxides (such as La_2O_3, Nd_2O_3 and Y_2O_3 powders, chemically pure, Tianyi Rare Material Ltd., Huizhou, China) as additives. The chemical compositions of main raw materials are given in Table 1 and the main chemical compositions of fibers are given in Table 2.

1.2 Characterization

In order to study the effect of rare earth oxide additives

Table 1 Chemical compositions of raw materials (wt.%)

Raw materials	CaO	MgO	SiO_2	Al_2O_3
Wollastonite	51.08	3.68	45.81	0.12
Talc	1.60	33.74	64.24	0.07
Quartz sand	0.27	0.02	99.05	0.27

Table 2 Main compositions of AES fibers (wt.%)

Samples	CaO	MgO	SiO_2	La_2O_3	Nd_2O_3	Y_2O_3
1#	29	6	62	0	0	0
L1	28.2	5.8	62	1	0	0
N1	28.2	5.8	62	0	1	0
Y1	28.2	5.8	62	0	0	1

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on the viscosity of the melts, the calcium magnesium silicate melts containing different rare earth oxides were prepared in induction furnace. The viscosity of melts were measured by a high temperature viscometer using the concentric cylinder method. The viscosity of powdered fragments of fibers was measured with a rotating crucible viscometer (RTW-10, KEXIANG Instruments Ltd., Anshan, China). About 100 g powdered fibers were melted in a graphite crucible in a furnace heated up to 1520 ºC. The Pt spindle was placed in the center of the crucible and 7 mm above the bottom of the crucible. After the furnace was set to required soaking schedule, the digital recording began.

Investigations of dissolution behavior for the mentioned fiber were carried out as shown in Fig. 1. After being ground, fragments of fibers about 50–100 μm in length and about 1 g in weight were laid in the teflon reactor with 1000 mL solution. The Gamble solution which simulates human lung fluid had the following composition: NaCl 6.415 g/L, $NaHCO_3$ 2.703 g/L, $MgCl_2{\cdot}6H_2O$ 0.212 g/L, Na_2HPO_4 0.148 g/L, $CaCl_2{\cdot}4H_2O$ 0.318 g/L, $Na_2SO_4{\cdot}2H_2O$ 0.179 g/L, sodium sulphate 0.180 g/L, sodium citrate 0.186 g/L, sodium lactate 0.175 g/L, sodium pyruvate 0.172 g/L, glycin 0.118 g/L. The runs were performed by 0–72 h. After each run, the fibers were removed from the solution, then rinsed with deionized water and dried at 37 ºC for 12 h in an oven before being weighed. After the solution was extracted from collection flask, the changes of the concentration of ions leached from fibers in the solution were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Haiguang Instruments Ltd., Beijing, China).

To determine the crystallization behaviors of soluble fibers, thermal analysis was carried out employing a Mettler Toledo STARe System (Mettler-Toledo Ltd., Leicester, U.K.), which was capable of performing thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) investigations simultaneously. The TGA and DSC experiments were conducted in controlled atmosphere of air at a flow rate of 50 mL/min. The TGA/DSC analyses were carried out from ambient temperature to 1000 ºC with heating rate maintained at 3 ºC/min without any holding time. The mass of the powdered sample used was adjusted at about 15 mg in each experiment. The fiber samples were firstly exposed at selected temperature in the range of 800–900 ºC in an electric furnace. After the thermal treatment the identity of phases has been examined by XRD using Cu Kα radiation with scanning speed of 10 (º)/min.

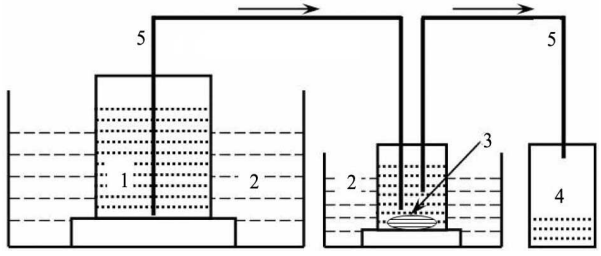

Fig. 1 Experimental device for dissolution process
1–Simulated lung fluid; 2–Water bath; 3–Fiber sample; 4–Collection flask; 5–Delivery

2 Results and discussion

2.1 Viscosity of melts

It is known that the AES fibers are produced generally by an electric melting alkaline earth silicate mixture of raw materials and then multi-wheels centrifuge thinning or blowing process. The suitable viscosity curve with temperature change would be in favor of fiberization of the melt. The viscosity of melt is dependent on the chemical composition of melt and temperature. The relationship curves of the viscosity vs. temperature of the calcium magnesium silicate melts with addition of some rare earth oxides are shown in Fig. 2.

From Fig. 2 two important observations can be made: it can be seen that the viscosities of all alkaline earth silicate melt decrease with temperature increasing. Furthermore, addition of La_2O_3, Nd_2O_3, Y_2O_3 into alkaline earth silicate melt remarkably decreases the viscosity. Besides, the viscosities of melts L1, N1 and Y1 are seen to increase in the order: L1>Y1>N1; and the viscosities of melts containing rare earth oxide decrease gradually with temperature increasing. The changes in viscosity of high temperature melts containing rare earth oxide indicate that rare earth ions behave as a network modifier of complex silicate anions in high temperature melts, which is in agreement with results of infrared and Raman spectra of silicate glasses containing rare earth ions[8]. Therefore, addition of some rare earth oxides into the calcium magnesium silicate mixture of raw materials is essential to maintain the significantly lower viscosity of high temperature melts that is needed for the formation of fibers.

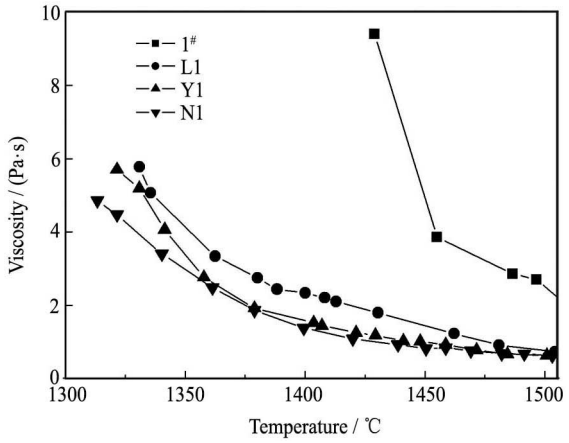

Fig. 2 Changes in viscosity of high temperature melts at different temperatures