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Study of the high purity and ultrafine silica fibre

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The effects of leaching time, temperature and the concentration of the acid solution on the purity of the drawn sodium borosilicate glass fibres were systematically studied. The high purity and ultrafine silica fibres were obtained by acid leaching method. The law of leaching non-siliceous constituents was found. Furthermore, leaching mechanism is discussed, which can be considered as a process of ion exchange and diffusion.

1. Introduction

The high purity, ultrafine silica fibre is one of the most excellent high temperature insulating materials, which is used as the baseline material for reusable surface insulation tiles of the space shuttle orbiter [1, 2], in addition, to other high temperature environments. The silica fibre made by the acid leaching method is of low cost.

Although the high purity, ultrafine silica fibre has already been made by acid leaching method in some glass systems [3–5], and several other techniques of leaching have also been developed [6, 7]. Up to now, no systematic research reports on the law of leaching non-siliceous constituents from glass fibre without phase separation and leaching mechanisms, etc. have been made. The purpose of the study was to ascertain the above essential questions such as the effects of original glass structure and composition, the temperature, leaching time and acid concentration on the purity of the fibres. Leaching mechanism is discussed on the basis of experimental results. From these, we can propose a theoretical basis for the design of original glass composition and best conditions for acid leaching.

2. Experimental procedure

The drawn sodium borosilicate glass fibres used in this study had the following composition in wt%: SiO_2, 55–75; B_2O_3, 20–35; Na_2O, 5–10. The glass fibres were then soaked in analytical reagent grade HCL solutions having normalities of 1, 1.5, 2.5, 4, 5, 6 and 6.5 for 30, 60, 90, 120, 150, 180 min at the different temperatures (50–100 °C), with period stirring. The ratios (in weight) of acid solution to the glass fibres was 50 and 100. After being exposed to the leachant, the fibres were washed in distilled H_2O until the wash solution became neutral. It was then baked in an oven at 100–120 °C.

The chemical composition of leaching fibres was analysed by different methods which are listed in Table I. The coordination number of B in original fibres was determined by nuclear magnetic resonance (NMR). Ramanru-1000 model Raman spectroscopy was used for the structure of the leaching fibres, and the 514.5 nm wavelength Ar^+ laser was chosen. The surface of leaching fibres was examined by scanning tunnelling microscope.

3. Results

3.1. Effect of structure and composition

The residual contents of non-siliceous constituents in different starting fibres, leaching ratio and structure of starting fibres are summarized in Table II. It is found that the more three fold boro coordination the borosilicate glass fibres have, the more the amount of non-siliceous constituents can be leached out, and the easy leaching order is Na_2O, $[BO_3]$, $[BO_4]$, Al_2O_3. This is

TABLE I Analytic methods of several constituents

Constituent	Analytic method
SiO_2	Weight
B_2O_3	Spectrometry and colorimetry for low content Volumetry for high content
Na_2O	Flame photometer
K_2O	Flame photometer
Al_2O_3	Colorimetry
Fe_2O_3	Colorimetry
TiO_2	Colorimetry
CaO	Atom absorptiometer
MgO	Atom absorptiometer

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TABLE II Relationship between content of non-siliceous constituents, leaching ratio and structure of starting fibres[a]

Materials	Na_2O	B_2O_3	Al_2O_3	Na_2O	B_2O_3	Al_2O_3	CN3 of B
	(wt %)			(Leaching ratio %)			(%)
C_1	0.00	0.22	0.16	100	99.38	83.63	64.50
C_2	0.00	0.27	0.18	100	99.24	79.01	56.8
C_3	0.00	0.12	0.10	100	99.70	83.24	72.5

[a] Leaching conditions: time 150 min; temperature 90 °C, and concentration 2.6 M, ratio (in weight) of acid solution to the fibres, 50.

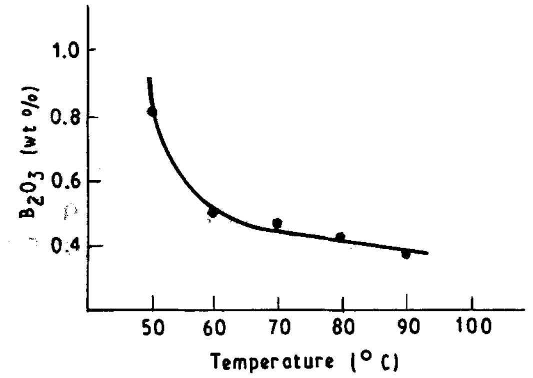


Figure 1 Effect of leaching temperature on contents of B_2O_3 in fibres.

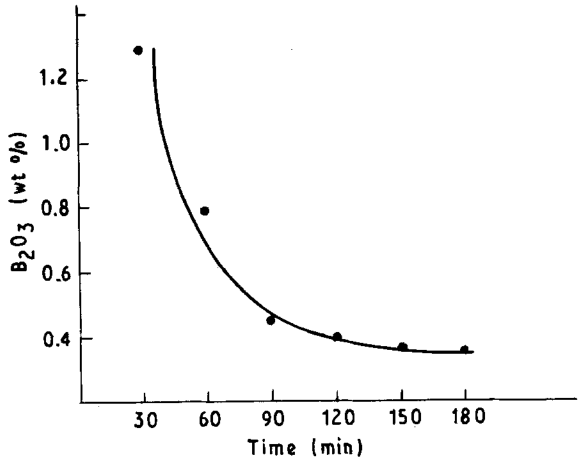


Figure 2 Effect of leaching time on contents of B_2O_3 in fibres.

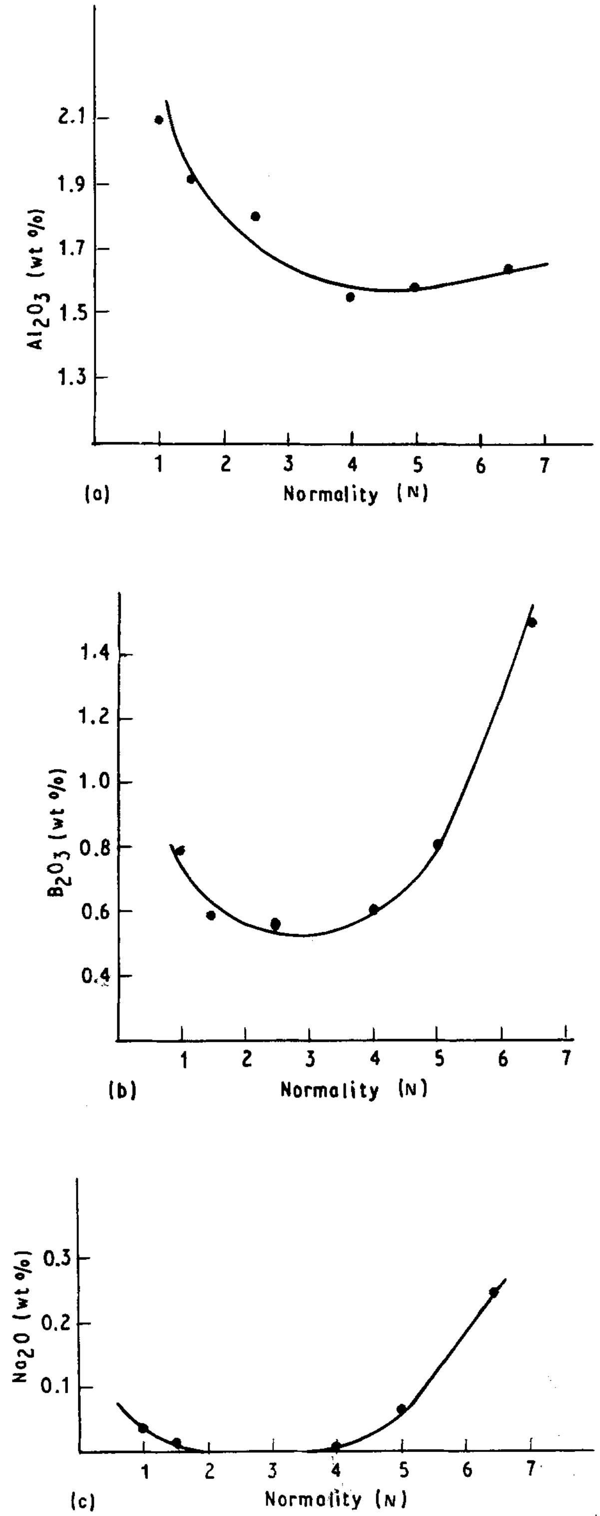


Figure 3 Effect of acid concentration on content of non-siliceous constituents in the fibres: (a) effect of acid concentration on content of Al_2O_3 in fibres; (b) effect of acid concentration on content of B_2O_3 in fibres; (c) effect of acid concentration on content of Na_2O in fibres.

related to the nature of non-siliceous constituents and their structure state in silica network.

3.2. Effect of temperature and leaching time

Figs 1 and 2 show the effect of temperature and leaching time on residual contents of B_2O_3 in final fibres, respectively. It is known that the residual content of B_2O_3 in the fibres also decrease continually, as the leaching temperature and time increase, and the speed gets slower and slower.

3.3. Effect of acid concentration

The residual content of non-siliceous constituents in the fibres as a function of acid concentration are shown graphically in Fig. 3. It is found that unlike the effect of temperature and leaching time, a minimum point appears on the curve of the residual content of non-siliceous constituents versus the acid concentration with the acid concentration increasing. The above interesting experimental results were attributed to the exchange reaction and the diffusion between the cations of non-siliceous constituents and H^+ ions.

The high purity silica (> 99.6 wt %) fibres (< 3 μm in diameter) can be obtained by acid leaching the drawn sodium borosilicate glass fibres under certain leaching condition.

4. Discussion

According to the following experimental results:

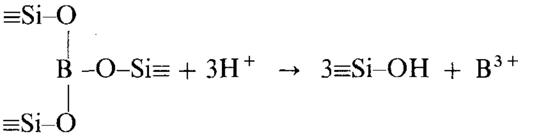
1. Fig. 4, shows scanning tunnelling micrograph of surface of leached fibres, from which it is clear that the pores on the surface of leached fibres were less than 1.5 nm, without large acid corrosion pore (4–15 nm) which was due to the dissolution of borosilicate glass fibres after phase separated.

2. Raman spectra analysis shows that the amount of broken bonds of leached fibres was 48%, and according to the exchange reaction ratio between Na^+ ions, B^{3+} ions in the fibres and H^+ ions in solution (1:1 and 1:3, respectively) the amount should be 46.4%, thus the analysis was approximate.

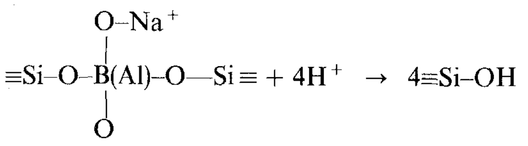
3. Fig. 5, shows the relation between the weight loss of leached fibres at 1300 °C for 10 h, and the residual contents of B_2O_3 in the fibres. As can be seen, the weight loss reduces as the residual content of B_2O_3 increases, i.e. the forming water in the fibres, including hydroxyl groups, increases as the residual content of B_2O_3 decreases, therefore the water in the fibres, including hydroxyl groups, was mainly formed by the exchange reaction between H^+ ions and B^{3+} ions, Na^+ ions.

Leaching mechanism can be considered as a process of the exchange and diffusion between B^{3+}, Na^+ ions and H^+ ions, i.e. H^+ ions in acid solution diffuse from the surface of the fibres into the interior and exchange with Na^+, B^{3+} ions, according to the following equations:

$$\equiv\mathrm{Si{-}O{-}Na} + \mathrm{H}^+ \rightarrow \equiv\mathrm{Si{-}OH} + \mathrm{Na}^+ \quad (1)$$



$$\underset{\equiv\mathrm{Si{-}O}}{\overset{\equiv\mathrm{Si{-}O}}{\mathrm{B}}}\mathrm{{-}O{-}Si}\equiv + 3\mathrm{H}^+ \rightarrow 3\equiv\mathrm{Si{-}OH} + \mathrm{B}^{3+} \quad (2)$$



$$\equiv\mathrm{Si{-}O{-}}\underset{\mathrm{O}}{\overset{\mathrm{O{-}Na^+}}{\mathrm{B}}}\mathrm{(Al){-}O{-}Si}\equiv + 4\mathrm{H}^+ \rightarrow 4\equiv\mathrm{Si{-}OH} + \mathrm{B}^{3+}(\mathrm{Al}^{3+}) + \mathrm{Na}^+ \quad (3)$$

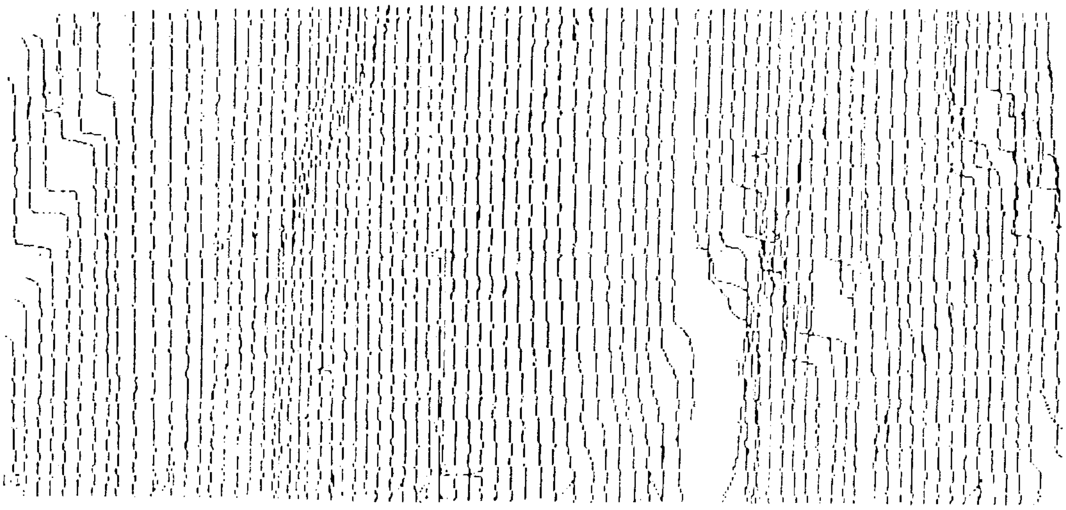


Figure 4 Scanning tunnelling micrograph of surface of leached fibres.

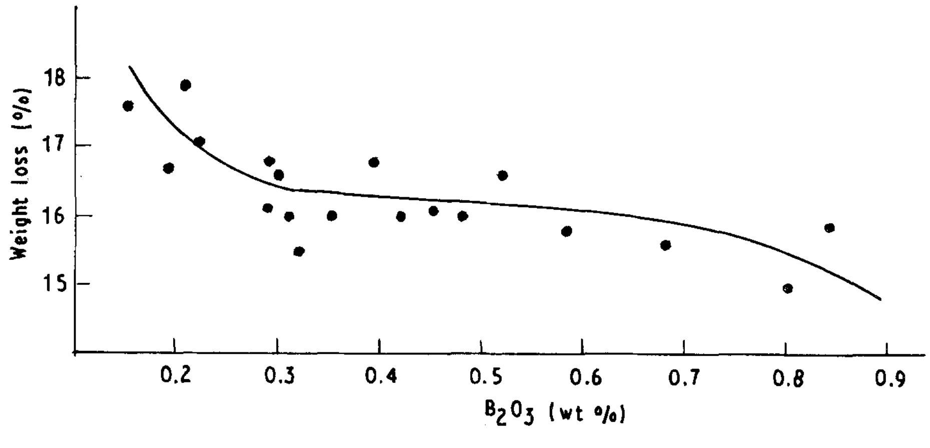


Figure 5 Relation between the weight loss of leached fibres at 1300 °C for 10 h and the residual content of B_2O_3 in the fibres.

and then, the exchanged $B^{3+}(Al^{3+})$ and Na^+ ions diffuse onto the surface of the fibres, then the solution, without apparent phase separation occurring during the course of drawing fibres. The leaching process was controlled by ion exchange reactions at the initial stage. As a result of the rich Si film layer formed on the fibre surface getting thicker and denser, which prevents ions from diffusing, especially H^+, the speed of the reaction was controlled by diffusing speed of the ions at final stage.

It is well-known that the rate of the ion exchange and diffusion increases and on the other hand, the rich Si film layer on the fibres surface gets thicker and denser, which prevents ions from diffusing, with acid concentration and temperature. When the acid concentration was low, the leaching process was governed by the exchange reaction, therefore, the residual content of non-siliceous constituents in the fibres decrease continually. When the acid concentration was high, the leaching process was governed by the diffusion reaction, on the contrary, the residual content of non-siliceous constituents increase. Hence a minimum point appears on the curve of the residual content of non-siliceous constituents versus the acid concentration. The same argument could be applied to explain the effect of temperature (see Fig. 1).

5. Conclusions

1. The high purity silica (> 99.6 wt %) fibres (< 3 μm in diameter) can be obtained by acid leaching of the drawn sodium borosilicate glass fibres under certain leaching condition.
2. The more three fold boro coordination the borosilicate glass fibre has, the larger the amount of non-siliceous constituents in the final fibres can be leached out, and the easy leaching order is Na_2O, $[BO_3]$, $[BO_4]$, Al_2O_3.
3. The residual content of non-siliceous constituents in the fibres also decrease continually, as the leaching temperature and time increases, and the speed gets slower and slower. A minimum point appears on the curve of the residual content of non-siliceous constituents versus the acid concentration with the acid concentration increasing.
4. Leaching mechanism can be considered as a process of ion exchange and diffusion, and the process is controlled by the ion exchange at the initial stage, and by the ion diffusion at the final stage.

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