

The ageing behavior of vacuum insulation panels with a new getter

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Abstract. The evacuated insulation technology of Vacuum Insulation Panels (VIP) enables approximately 5-8 times higher thermal resistance than conventional thermal insulation at similar thickness. The gas permeating through the envelope material and the heat sealing area may also play the most important role in thermal conductivity. The getter is required to be integrated into core materials in order to absorb gases and water vapor. In this paper, a new getter (named as A101b) with mixture powder was prepared. Switching to the A101B getter added alloy powder, as a result, deterioration speed of Delta K per day decreased 40%. With smaller pore size and less outgassing, the delta K per day of glass wool VIPs is the lower than glass fiber core material VIPs.

Key words. Vacuum insulation panel, thermal conductivity deterioration, getter.

1. Introduction

Increased ecological concerns and energy issues have prompted policy makers around the world to set stringent standards in order to improve energy performance of buildings and appliances. Since effective thermal insulation can reduce energy consumption rates and CO₂ emissions dramatically. There is a need to develop materials with enhanced thermal insulation characteristics. The evacuated insulation technology of Vacuum Insulation Panels (VIPs) enables approximately 5-8 times higher thermal resistance than conventional thermal insulation at similar thickness. Hence, equipped with super insulation characteristics and space saving attributes, VIPs are widely recognized as a promising solution for achieving enhanced energy efficiency requirements, set by policy makers [1].

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Basic structure of VIP consists of highly open porous core structure with very low thermal conductivity, encapsulated within an envelope material under vacuum. The envelope material would have higher thermal conductivity than the core material, while moisture/air absorbers such as getters/desiccants are often present in core. Types of core material differ depending on the type of application. For building insulations, VIPs with silica powder type core material are normally used due to long service life (25 years) [2]. Fibrous core materials such as glass fibers with compatible getters are traditionally used in refrigeration insulation due to its lower cost and ultra-low thermal conductivity under evacuated conditions compared to powder or foam type materials [3].

In this paper, the outgassing and sorption characteristics of glass fiber and glass wool core materials was investigated. In addition, microstructure of the A101B getter consisting of 85% of calcium oxide powder and 15% of Cu-Mn-Ce-O powders and the aging behavior of VIPs were investigated. The objective of this work was to prolong service life of VIPs and investigate the effect of getter on the thermal conductivity of VIPs with different core materials.

2. Materials and methods

2.1. VIP preparation

Table 1 shows the serial number. Four kinds of VIPs were prepared with two types of core materials and two types of getters. All the core materials were processed by wet method. The envelopes were composed of 15 μ m thickness nylon, 12 μ m thickness vacuuming metalized polyethylene terephthalate, 7 μ m thickness aluminum foil and 50 μ m thickness low-density polyethylene. The sheets were cut into 300X300mm and stacked into compression thickness of 12mm dried for 1h at 230???. Then, the core materials were put into the envelope, evacuated to pressure less than 0.01Pa, heat sealed to make VIP samples.

Table 1 The structure composition of VIPs

Distinguish	Core material	Getters/ composition
1#	Glass fiber	A101b/CaO/ Cu-Mn-Ce-O
2#	Glass wool	A101b/CaO/ Cu-Mn-Ce-O
3#	Glass fiber	CaO
4#	Glass wool	CaO

2.2. VIP Characterization

The increase of inner pressure in VIPs, initially at a sufficiently high vacuum, is considered to two factors: (1) gas permeation through the envelope, (2) outgassing from the core material[4]. An analysis on the outgassing of the core materials has been performed by quadruped mass spectrometer. Table 2 shows the test parameter.

Table 2 The test parameter of outgassing analysis

Test pressure(Pa)	Test range (m/z amu)	Test model	Test temperature (°C)	relative humidity (RH%)
1.4×10^{-4}	1~100	HIDEN HMT RC101	25	40

The microstructure of the getters were checked by SEM(JEOL JSM-6360).

Gas pressure increasing in the VIP resulted from gases released from the inner core material and the ambient air can permeate through the sealing layers at the side and through the surface of the envelope[4], [5]. In order to examine getter, the aging test were processed at 80 and 65% RH for 180 days. The thermal conductivity was checked by heat flow meter thermal conductivity instrumentation (Netzsch HFM 436, accuracy is ± 1 to 3%).

3. Results and discussion

3.1. VIP initial thermal conductivity

Initial thermal conductivity of VIPs was determined by heat flow meter thermal conductivity instrumentation. The temperatures of hot plate and cold plate are 38 and 10, respectively. And the difference of the temperature between hot plate and cold plate was 28, and the mean temperature was 24. The result was shown in Table 3.

Table 3 The result of VIP thermal and physical properties

Series	Length mm	Width mm	Thickness mm	Density kg/m^3	Initial thermal conductivity mW/(mk)
1#	301	303	11.77	275	1.241
2#	303	300	12.01	238	1.429
3#	300	301	11.85	271	1.217
4#	301	300	12.23	241	1.405

3.2. Result of core material outgassing test

The result of glass wool and glass fiber core material outgassing test is shown in Figure 4. The results of outgassing test of Glass wool core material and glass fiber core material shows in Figure 1. The outgassing volume and gas composition of two kinds of core material vary greatly under a vacuum degree of 1×10^{-4} pa. The emissions from glass wool core material and glass fiber core material both mainly contains hydrogen, water vapor, carbon monoxide, nitrogen and carbon dioxide and a small amount of hydrocarbon gas, while the emissions from glass fiber core material contain large number of small molecules of hydrocarbon gas. The organic solvent

was sprayed on the surface of the glass fiber during the forming process, which is the source of the hydrocarbon gases. The quantitative analysis result shows the amount of release gases of glass fiber is 2-4 times as high as glass wool.

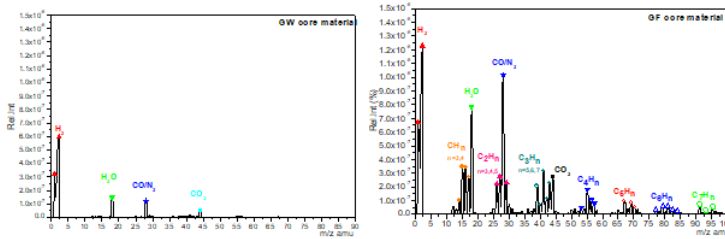


Fig. 1. The result of GW and GF core material outgassing test

3.3. Microstructure comparison of getters

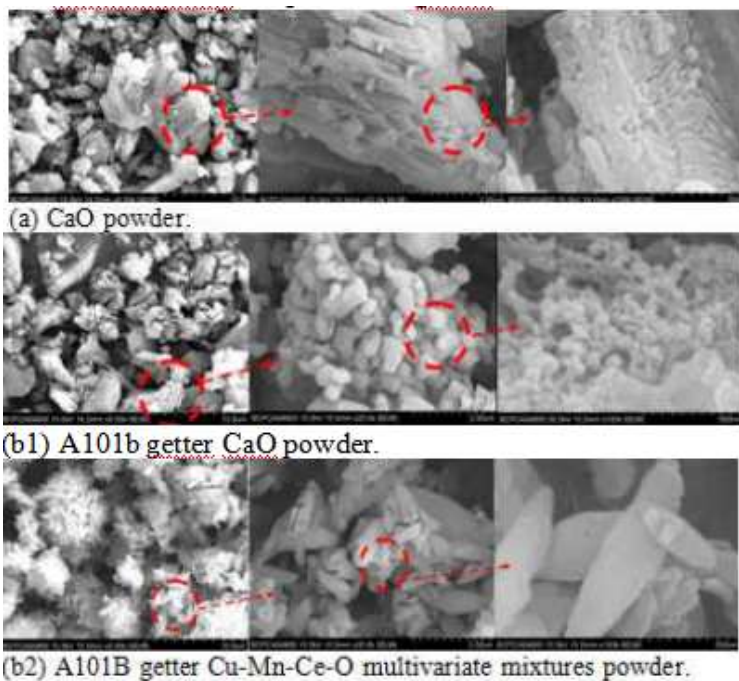


Fig. 2. SEM images of the two type getter

Two type getter SEM images are shown in Figure 2. The CaO getter powder has a particle size range from $1.0\mu\text{m}$ to $10.0\mu\text{m}$ (see Figure 2 (a)). The A101b getter powder is composed of two powder: Calcium Oxide powder with a particle size ranging from $1.0\mu\text{m}$ to $6.5\mu\text{m}$ (see Figure 2(b1)), Cu-Mn-Ce-O multivariate mixtures powder with a particle size ranging from $0.1\mu\text{m}$ to $1.0\mu\text{m}$ (see Figure 2 (b2)). The

process of gettering obtained with three steps: physical adsorption, chemical reaction and chemisorptions[6]. The A101B getter powder with smaller partial size and higher specific surface area as shown in Figure 2, has a better performance on the sorption speed and the sorption quantity.

3.4. Accelerated aging test

Heat transfer in the VIP takes place by three methods: the solid conduction through skeleton of the core, the gas conduction through residual gas, and the radiation. In a VIP, the k(center of panel, marked as cop) can be expressed as the sum [7], [8]:

$$k_{cop} = k_s + k_g + k_f \dots \dots \dots (1)$$

where k_g , k_s and k_r are the gas, solid and radiative conductivities, respectively.

Both k_s and k_r strongly depend on the packing density which depends on the mechanical pressing load. The core material is pressed at about 0.1 MPa as far as the core must withstand the atmospheric pressure. However, the initial performance improvement of VIPs has been limited to the suppression of radiation. The density of a VIP is almost unchanged in the first decades other than the addition to leakage. The high thermal performance of VIPs is mostly achieved by reducing the gas thermal conductivity via reduction in pore pressure of core material; and the most effective reduction is achieved at total vacuum process, when gas thermal conductivity could approach zero [9], [10]. The gas conductivity k_g is derived b as[5],[

$$L_m = 2.19 \cdot 10^{-5} TP \dots \dots \dots (2)$$

where T is temperature in K and P is the gas pressure in Pa. In low pressure condition, the mean free path is larger than the pore in core structure. Gas conduction mechanism is totally varied by the Fourier’s law. Smoluchowski expressed heat flux conduction as [11]

$$K_g = k_{g0} \cdot \Phi(\Phi + 2\beta) \dots \dots \dots (3)$$

where k_{g0} is the standard air thermal conductivity, for air at room temperature, $k_{g0} \approx 0.026 \text{ W/m}\cdot\text{K}$. Φ is the pore size of porous material in m and β is a function of the constant pressure to constant volume specific heat ratio. For air, β can be expressed as

$$\beta = (5.35 \cdot 10^{-5}) \cdot TP \dots \dots \dots (4)$$

The gas conductivity k_g is derived by combining Eqs. (2) and (3) as

$$k_g = \frac{k_{go}}{1 + \frac{0.032}{P\phi}} \dots\dots\dots (5)$$

The outgassing of the inner core material greatly influences the inner pressure in the short-term and long-term service life. The gas permeating through the envelope material and the heat sealing area may also play the most important role in thermal conductivity deterioration. In particular, the outgassing from core materials may produce disastrous influence on the thermal conductivity of VIPs, apart from the gas thermal conductivity due to the effect of gas within the pore space[12].

Based on the above getter and core material specifications, a comparative accelerated tests validation was performed in the 80 °C-65%RH condition. The results of change in thermal conductivity are shown in Figure 3. In Table 4, it can be seen that the change in thermal conductivity from 0 day to 180 days. Delta K per day was checked as 0.01mW/(mk)(sample 1#), 0.06 mW/(mk) (sample 2#), 0.016mW/(mk) (sample 3#), 0.012 mW/(mk) (sample 4#). The thermal conductivity of sample 3# increased fastest as a result of outgassing and big pore size of glass fiber core material. Switching to the A101B getter added alloy powder, as a result, deterioration speed of Delta K per day decreased 40%(see sample 1# and sample 3# in Figure 3). With smaller pore size and less outgassing, the delta K per day of glass wool VIPs is the lowest see comparative sample 2# and 4# in Figure 3.

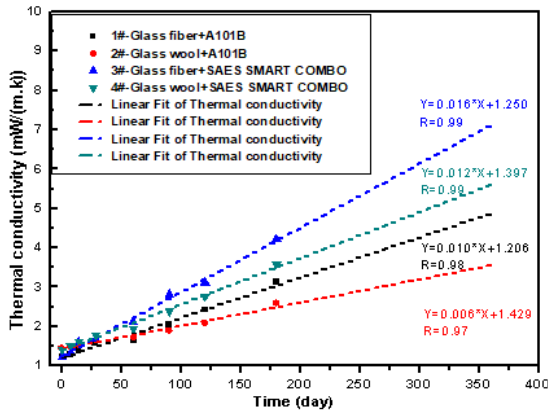


Fig. 3. Test results and prediction of the thermal conductivity for accelerated aging test

4. Conclusions

The quantitative analysis result shows the amount of release gases of glass fiber is 2-4 times as high as glass wool. The A101B getter powder with nanometer mixture powder and higher specific surface area, has a better performance on VIP thermal

conductivity deterioration. The thermal conductivity of sample 3# deteriorated faster than sample 4# as a result of outgassing and big pore size of glass fiber core material. Switching to the A101B getter added alloy powder, as a result, deterioration speed of Delta K per day decreased 40%(see sample 1# in Figure 3).

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