Acta Technica 62 (2017), No. 5A, 255–262

Preparation and sorption properties characteristics of a mixture getter for vacuum insulation panels

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Abstract. Vacuum insulation panels (VIPs) with their extra-thin thickness but a distinguished thermal insulating property, are widely used in the applications such as refrigerators, building sector, and aeronautics and astronautics. The getter is required to be integrated into core materials in order to absorb gases and water vapor released from glass fiber or glass wool itself and permeated through film and heat seal layer . In this paper, a new type getter (marked as A101B) consisting of 85% of calcium oxide powder and 15% of Cu-Mn-Ce-O powders was investigated. In addition, the component and microstructure of the A101B getter were investigated. A high magnification SEM image of the Cu-Mn-Ce-O multivariate mixtures powder reveals that acerose particles stack to porous structure. These pore ranges from about several nanometer to several hundreds nanometer in diameter, providing high surface energy.

Key words. Vacuum insulation panels, getter, acerose particles, high surface energy.

1. Introduction

Vacuum insulation panels (VIPs) with their extra-thin thickness but a distinguished thermal insulating property, namely thermal resistance about 10 times higher than that of the conventional insulators like polyurethane foams and polystyrene, are widely used in the applications such as refrigerators, building sector, and aeronautics and astronautics [1], [2]. VIP makes use of vacuum to suppress the heat

[1]Acknowledgment - This work was supported by Major Achievements Transfer Projects of Jiangsu province (BA2013097), National Project (2015DFI53000), and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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transfer from gaseous conduction, just like in conventional Dewar and Thermos flasks [3]. A VIP is composed of core material, envelope material and getter or desiccant. Each component has its respective functions in this multi-unit system: the core material provides strength against the external atmospheric pressure and endows the thermal insulating property; the envelope material maintains the inner vacuum and provides a long-time service life; the getter or desiccant adsorbs various gases flowing into the vacuum and releasing from core materials [4]. Glass fibers or wool are commonly used as VIPs core material due to their excellent molding properties, low density, outstanding thermal and acoustic insulation properties, superior chemical and thermal stability; the resulting VIPs are properly known as glassfibre or glass wool VIP [5].

Therefore, the getter is required to be integrated into core materials in order to absorb gases and water vapor released from glass fiber or glass wool itself and permeated through film and heat seal layer[6]. In a traditional VIP, a getter, for example SAES SMART COMBO getter, is composed of Calcium Oxide and cobaltous oxide mixture powder. Small inorganic molecular ,such as CO_2, O_2, H_2, are absorbed by the above powder. However, much organic molecular added in core material forming process releases from glass fiber in vacuum condition, CxHy (molecular weight at 16-95) and CO mostly. The oxidations of the copper and manganese was employed as the catalyzer to promote oxidation processes of the C_xH_y and CO [7]. Research indicated that the Cu-Mn mixed oxidation obtains better catalytic activity compared to the pure CuO catalyzer. Meanwhile, its catalytic activity in redox reaction was improved with the addition of CeO_2[8]. In the redox reaction, C_xH_y and CO were oxidized to CO_2 and H_2O, further absorbed by the CaO.

In this paper, the sorption characteristics of a new type getter (marked as A101B) consisting of 85% of calcium oxide powder and 15% of Cu-Mn-Ce-O powders, was investigated. In addition, the component and microstructure of the A101B getter were investigated.

2. Materials and methods

2.1. A101B getter preparation

The A101B getter is an binary mixture which is composted of calcium oxide and Cu-Mn-Ce-O as shown in Figure 1. Small partical size and high specific surface area calcium oxide powder obtained with the method of vacuum sintering , where precise temperature setting was necessary, has a high surface activity and admirable getter capacity. Cu-Mn-Ce-O multivariate mixtures were prepared by steps of high-temperature sintering, surface modification and vacuum heat treatment.

2.2. Sorption properties test of the getter

As two of the indexes of the getter materials, the sorption speed and the sorption quantity showed their important effects on evaluating its gettering ability. According to the standards of **ASTM F798-97(2002)[8]and the GB/T 8763-88[10],**

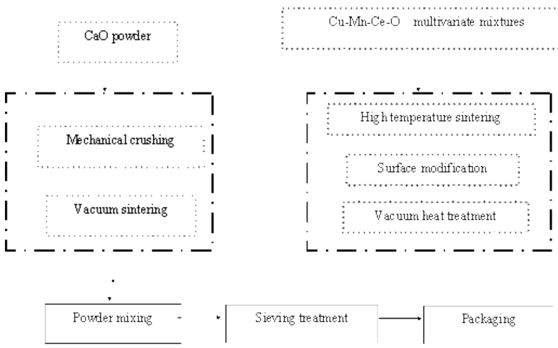


Fig. 1. The process of A101B getter preparetion

the sorption speed was the tested gas volume (cm3s-1g-1) absorbed by per unit mass of getter materials at a certain temperature in the unit of time. And, the sorption quantity was defined it that the total inhaled gas before the sorption speed decreasing to one certain eigenvalue. Meanwhile, the method for testing the getter ability consisted of two ways: the method of constant pressure and the method of constant volume. And, the method of constant pressure was mainly ultilized in this investigation, whose measurement mechanism was as follows. A pressure difference occurred in the vacuum chambers(Pm and Pg) at end of a capillary tube with a certain conductance, when a stream of molecular gas flowing through it. And, the sorption speed and the sorption quantity of the sample were resulted by recording this difference, where its testing system was shown in Figure 2.

The detailed test processes were as follows. The fixation process of getter materials in the sample chamber of the test system. For testing, the turbo-molecular pump and mechanical pump were utilized to reduce the system pressure and controlled its vacuity below a value of 8×10-6 Pa. After the vacuity arriving, the tested gas with a high purity of 99.999% was injected in the Pg sample chamber and controlled at a certain value by governing the micrometering valve. For testing with the method of constant pressure, the relationship of the sorption quantity(Q) and the sorption speed(S) was shown in equation (X1) and (X2), where, the S was the sorption speed(cm3 s^{-1} g^{-1}), the P_m was the pressure of the gas input chamber (Pa), the $P_g$was the pressure of the sample chamber (Pa), the F was the conductance coefficient(cm^3 s^{-1}) and the m represented for the getter mass(g)[9], [10].

$$Q = F/m \int_0^t (P_m - P_g)\, dt \tag{1}$$

$$S = F\,(P_m - P_g)\,/P_g \cdot m \tag{2}$$

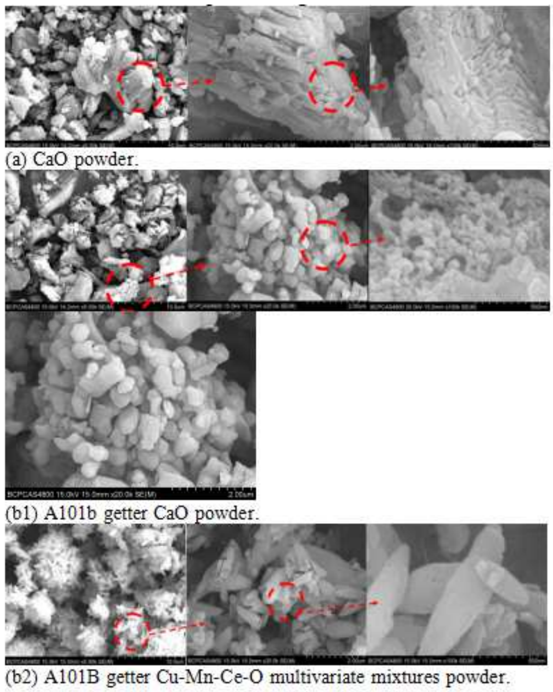


Fig. 2. The diagram of gettering test system of the method of constant pressure

2.3. Microstructure and composition

The microstructure and composition of the core materials were checked by SEM (JEOL JSM-6360) and X-ray diffraction(XRD, Bruker D8 Advanced) respectively.

3. Results and discussion

3.1. Sorption properties

As the sorption properties data of two types getter shown in Figure 3, the A101B getter has a significant improvement for the sorption speed and unit sorption quantity of H_2O, O_2, CO_2, CO and H_2. CeO_2 /CuO blends will improve the oxidative activity for CO and H_2, compared to the single component CuO [11]. Under the reaction conditions, electron transfer occurs within $CuMn_2O_4$[12]:

The cyclic change of the valence state of Cu and Mn is conducive to the oxidation-reduction .

The sorption properties of hydrocarbon is difficult to check because of its complex composition. In the following, the author will explain sorption mechanism of hydrocarbon gas by A101B getter. CeO_2 is an effective catalyst for hydrocarbon oxidation. Low valence cerium and oxygen deficiency occur in the surface of the CeO_2 at a vacuum or restore condition, which has excellent catalytic function in

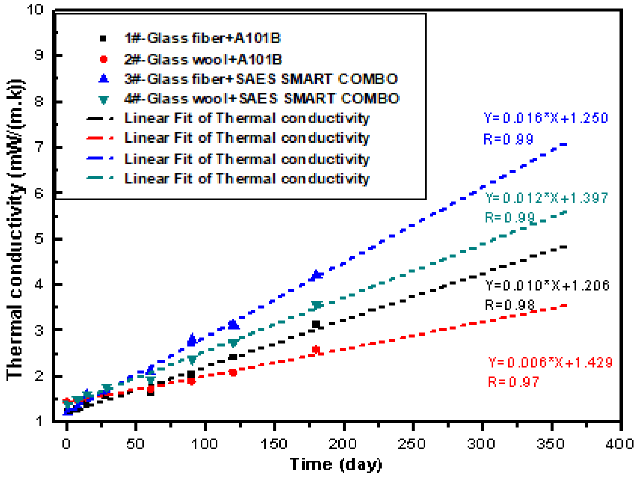
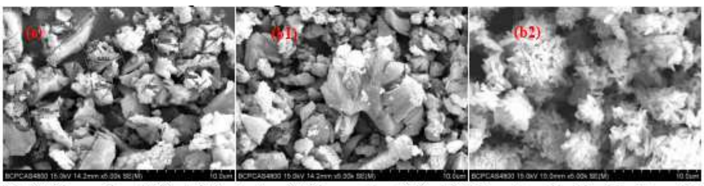


Fig. 3. The curve of Sorption properties

oxidation-reduction and charge exchange Reaction [13]. In the oxidation-reduction, C_xH_y were oxidized to CO_2 and H_2O , further absorbed by the CaO.

In a traditional VIP, a getter, for example CaO getter, is composed of Calcium Oxide and cobaltous oxide mixture powder. Small inorganic molecular, such as CO_2, O_2, H_2, are absorbed by the above powder. However, much organic molecular added in core material forming process releases from glass fiber in vacuum condition, CxHy (molecular weight at 16-95) and CO mostly.

3.2. Microstructure comparison of getters



(a) CaO powder (b1) A101b getter CaO powder (b2) A101B getter Cu-Mn-Ce-O multivariate mixtures powder.

Fig. 4. SEM images of the two type getter

Two type getter SEM images are shown in Figure 4. The results are discussed as follows.

(i) The CaO getter powder has a particle size range from 1.0μm to 10.0μm (see Figure 4 (a)). Block and non-porous structure of the particles ,as a result, possesses smaller specific surface area and ordinarysorption property.

(ii) The A101B getter powder is composed of two powder: Calcium Oxide powder with spheroidal particle and its size ranging from1.0μm to 6.5μm (see Figure 4 (b1)), Cu-Mn-Ce-O multivariate mixtures powder with acerose particle and its size ranging from0.1μm to 1.0μm (see Figure 4 (b2)).

(iii) As shown in Figure 4 (b1), the Calcium Oxide particles are porous structure, in which many nano-porous and nano-particles were obtained. Massive nano-porous and nano-particles play an important role on high surface energy and sorptionproperty.

(iv) In Figure 4 (b2),a high magnification SEM image of the Cu-Mn-Ce-O multivariate mixtures powderreveals that aceroseparticles stack to porous structure . These pore ranges from about several nanometer to several hundreds nanometer in diameter, providing high surface energy.

The multivariate mixtures powder composition has been identified as CuO-CeO_2-$CuMn_2O_4$mixed powder by XRD (see Figure 5). The process of gettering obtained with three steps: physical adsorption, chemical reaction and chemisorptions. The A101B getter powder with smaller partical size and higher specific surface area as shown in Figure 4, has a better performance on the sorption speed and the sorption quantity.

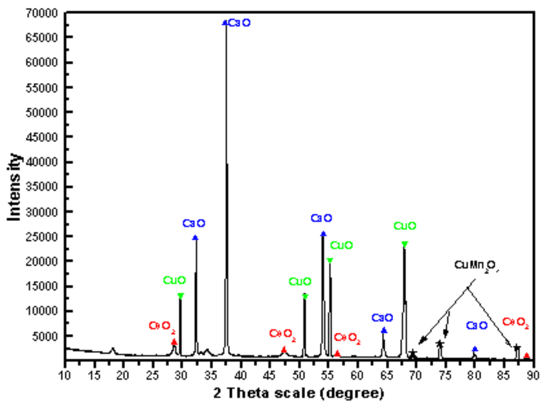


Fig. 5. XRD result of A101B sample

4. Conclusions

The A101B getter is an binary mixture which is composted of calcium oxide and Cu-Mn-Ce-O as shown in Figure 1. Small partical size and high specific surface area calcium oxide powder obtained with the method of vacuum sintering, where precise temperature setting was necessary, has a high surface activity and admirable getter capacity. A high magnification SEM image of the Cu-Mn-Ce-O multivariate mixtures powder reveals that acerose particles stack to porous structure . These pore ranges from about several nanometer to several hundreds nanometer in diameter, providing high surface energy.the TheA101B getter has a significant improvement for the sorption speed and unit sorption quantity of H_2O, O_2, CO_2, CO and H_2.

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Received November 16, 2017