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Research paper

Room temperature and high temperature sealing properties and compression properties of compressive gaskets made of micrometric vermiculite particles

A.N. Nguyen [a,b], L. Mirabel [b], L. Duclaux [a,*], L. Reinert [a], P. Dehaudt [b], J.F. Juliaa [b,c], A. Beziat [b]

[a] Univ. Savoie Mont Blanc, LCME, F-73000 Chambéry, France
[b] CEA/DEN/DTEC Laboratoire Maestral F30207 Bagnols sur Cèze, France
[c] Technetics Group France, 90 Rue de la Roche du Geai 42029 Saint-Etienne, France

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ABSTRACT

Vermiculite gaskets obtained by pressing vermiculite powders in the range of 17.7–80 MPa, were studied for their sealing (leak rate measurements) and compressive properties (compressibility and resiliency). The *in plane* permeability at room temperature was found to decrease strongly through increasing elaboration pressure, that reduced both the median pore radius (<30 nm) and the macropore volume fraction (<45%), measured by mercury intrusion. After annealing at temperatures of up to 600 °C, the *out of plane* permeability (measured at room temperature) was increasing from $\sim 10^{-20}$ (at 200 °C) to $\sim 10^{-24}$ due to the increase in anisotropy related to the densification and the formation of interlayer bonds. The global leak rate was found to be determined exclusively by the contact leak rate and independent of the material's permeability. The leak rates measured at room temperature were also found to be dependent on the gasket's resiliency values. The global helium leak rate (2.5×10^{-2} $\mathrm{atm \cdot cm^3 \cdot s^{-1} \cdot m^{-1}}$, for 35 MPa working pressure, under 5 bar helium pressure) was relied neither on the working temperature (25 °C to 800 °C) nor the material porosity for gaskets pressed at 200 °C and 80 MPa. The resiliency (~5%) and compressibility (9%) values of these gaskets were reduced, as heating the materials to 800 °C due to the densification induced by both pressure and temperature, increasing their rigidity.

1. Introduction

Before the 1990s, asbestos was one of the main materials used to build compressive gaskets for high temperature application (up to 800 °C), until its trade and use were banned outright due to the toxicity of inhalation of asbestos dust (Choiron et al., 2011). Graphite can substitute asbestos material in compressive gaskets, thanks to its interesting mechanical properties, but its temperature use is limited to 400 °C–500 °C because of its oxidation. Glass gaskets are used at high temperature but their main disadvantages lie in their adhesion to the support and the difficulties to disconnect the gaskets from their support (metal or ceramic) after the heating cycle at room temperature (Mahapatra and Lu, 2010). Thus, due to their thermal compatibility, an absence of adhesion to the support at high temperature and a certain compressibility, clay minerals (mainly vermiculite or mica) can be applied advantageously as compressive gasket materials with or without additives. Films of vermiculite or mica (mica paper) can both be formed by roll forming with chemical additives (binder, etc.) in order to prepare (compressive) gaskets. However, the presence of an organic binder can limit the application temperature to the temperature of decomposition of the binder.

Two sorts of mica: phlogopite and muscovite particles are widely applied in the preparation of compressive gaskets (Simner and Stevenson, 2001; Chou et al., 2002, 2003; Bram et al., 2004; Chou and Stevenson, 2004; Fergus, 2005; Chou and Stevenson, 2009). The main advantage of vermiculite upon mica is the possibility of layer exfoliation, which is supposed to give additional elasticity and compressibility to the compressive gaskets. Moreover, vermiculite can withstand temperature heating up to 800 °C, without any main change in its layered structure. Due to its ability to exfoliate (separation of the layers) by thermal shock or chemical reaction, and its thermal compatibility until 800 °C, vermiculite has been extensively used as material for high temperature compressive gaskets in many applications (Hoyes et al., 1998; Fergus, 2005; Batfalsky et al., 2006; Dunn et al., 2006; Hoyes, 2007; Wiener et al., 2007; Rautanen et al., 2009).

For a compressive gasket, the leak depends firstly on the path leak at the contact with the support, and secondly on the permeability through the materials if the contact leak is weak enough. The gasket materials need to be compressed at the initial screwing in order to accommodate the geometrical defects (surface roughness) of the support surface.

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[*] Corresponding author at: Université Savoie Mont Blanc, LCME, Campus de Savoie Technolac, 73376 Le Bourget du Lac, Cedex, France. Tel./fax: +33 4 79 75 88 05.
E-mail address: laurent.duclaux@univ-savoie.fr (L. Duclaux).

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Thus, the materials should possess the ability to strain in order to adopt the shape of the fine roughness of the sealing support. The gasket may also accommodate the small motion of the support during its life cycle. Thus, elastic mechanical properties are required.

The leaks of a pure mica compressive gasket made of paper (particles of 50 μm average 50 μm size) are usually found in the range of 10^{-1}–10 $\mathrm{sccm\cdot cm^{-1}}$ (i.e., $1.6 \cdot 10^{-3}$–$1.6 \cdot 10^{-1}$ $\mathrm{atm\cdot cm^{3}\cdot s^{-1}\cdot cm^{-1}}$) under compressive stress lower than 6 MPa and at temperature in the range of 25–800 °C. The tightness of the compressive mica gaskets is known to be controlled by the contact between the sealing material and the metallic or ceramic surface support. In order to improve the contact at the interface, flexible soft layers made of melted glass (Bram et al., 2004) or silver (Chou and Stevenson, 2009) on the mica surface have been developed and tested. As an example, the infiltration of phlogopite mica by $Bi(NO_3)_3$ or H_3BO_3 glass has successfully decreased the leak rate to almost $5 \cdot 10^{-4}$ $\mathrm{sccm\cdot cm^{-1}}$ (i.e., $8.3 \cdot 10^{-6}$ $\mathrm{atm\cdot cm^{3}\cdot s^{-1}\cdot cm^{-1}}$) after 15 cycles in the range of 100–800 °C (Chou and Stevenson, 2004). The last generation of vermiculite based gaskets developed by Flexitallic Company ("Thermiculite® 866") was pretended to be prepared without any organic binder (Hoyes, 2007; Hoyes and Rautanen, 2013). They contain few talc particles and can resist up to 800 °C (Hoyes, 2007). Upon 100 mbar of hydrogen and a compressive stress of 4–8 MPa, the leak rate was found to be close to 1–$3 \cdot 10^{-1}$ $\mathrm{atm\cdot cm^{3}\cdot s^{-1}}$ (Rautanen et al., 2009). Upon 15 mbar of a mixture of N_2–H_2 (50/50 vol.) and a compressive stress of 0.4 MPa, the leak rate per unit length of gasket was found to be close to 10^{-4} $\mathrm{atm\cdot cm^{3}\cdot s^{-1}\cdot cm^{-1}}$ (Rautanen et al., 2014).

In a previous work (Nguyen et al., 2014), the possibility to obtain vermiculite materials by uniaxial pressing of sonicated micrometric powders was demonstrated without any binder addition. In this paper, we have investigated the sealing properties of this new vermiculite gasket made of pressed small vermiculite particles (micronic and submicronic) without any binder. The sealing properties were studied in relation with the material texture. The permeability leaks (*in plane* direction and *out of plane* direction) and the surface leaks were determined as a function of pressure and the thermal treatment temperature. Moreover, some mechanical properties were studied (compression ratio and resiliency) in order to better understand their impact on the leak rate.

2. Experimental

2.1. Vermiculite powders

The starting vermiculite (Granutec E originating from Yuli China) was purchased from CMMP French Company and was used as received (millimetric plates). Potassium chloride (99%, Chimie Plus) was used to saturate the vermiculite before sonication. Hydrogen peroxide (H_2O_2, 35%, ACROS) was used to prepare suspensions of vermiculite. After potassium exchange, the average chemical composition of half a lattice cell calculated from elemental analysis was $(Si_3Al_1)\ (Mg_{2.62}Fe_{0.32}Ti_{0.06})\ O_{10}(OH)_2K_{0.61}$.

The K-vermiculite material was chosen because a weakly hydrated initial material was required in order to improve the stability in further heat treatment and in particular to avoid water release from the gasket during heat treatment. Moreover, previous studies have shown that K-vermiculite can be easily delaminated and micronized by sonication at 20 kHz in hydrogen peroxide solution (Nguyen et al., 2013) and then compacted in solid materials under pressure without any binder (Nguyen et al., 2014).

The vermiculite (0.4 mm mean diameter size, weighted amount of 0.55 g or 3.85 g) was sonicated at room temperature in 55 mL hydrogen peroxide (35%) in a "Rosett" type glass double-jacketed reactor cooled at 25 °C by circulation of a cryogenic fluid, using a Sonotrode (20 kHz, 350 W, Ti ultrasonic probe, Sonics and Materials, 43 mm amplitude, 56 W acoustic power) in order to produce small particles (Nguyen et al., 2013; Ali et al., 2014; Nguyen et al., 2014). The solid/liquid (S/L) ratio and the sonication time were varied in order to modify the particle size distributions. Powders were obtained by sonication of vermiculite dispersions prepared at two different S/L ratios (7% and 1%) during different sonication times (1 h, 5 h and 12 h).

The particle size distributions of the dispersions were measured with a Mastersizer 2000 particle size analyser (Malvern Instruments, range 0.02 μm to 2000 μm).

2.2. Elaboration and structure

The vermiculite powder (about 500 mg) was pressed at room temperature or at 200 °C under various pressures for 3 h (Nguyen et al., 2013, 2014) in the form of cylinders (13 mm external diameter, about 2 mm thickness), either as a full pellet for measurement of the *out of plane* leak or including a central hole of 5 mm diameter for measurement of the radial leak. For hot-pressing, the powder was first pressed at room temperature for 15 min. The pressure was maintained as the mould was heated at 200 °C (4 °C/min, for 45 min). After 2 h at 200 °C, the pressure was released and the sample was turned out of the mould. The formed materials were then thermally heat treated in the range of 400 °C–1000 °C for 10 h in a muffle furnace (4 °C/min).

2.3. Measurement of total leak rate and in plane permeability leak rate

The gaskets were introduced in the circular groove of a metallic immovable holder, constituting a part of a mould manufactured in a nickel based superalloy ($NiCr_{20}Co_{13}Mo_4Ti_3A$, named Waspaloy) and pressed between the two faces of this mould (Fig. 1). A metallic porous cylinder from the same nickel based alloy was introduced into the hole of the gaskets (Fig. 1). The complete mould device and gaskets were then compressed at 35 MPa using an MTS press (Insight 50) for 1 h for the room temperature test or for at least 7.16 h for the test at 800 °C (including 1 h at room temperature, 2.66 h min for the heating ramp, 0.5 h for the plateau at 800 °C, and 3 h or 18 h for the cooling to room temperature).

Before measurements the internal volumes and the porous metallic cylinder were degassed under a primary vacuum. A constant pressure of 5 bar of helium (99.95% purity) was applied in the centre of the drilled gasket (Fig. 1). After the helium injection, the amount of gas crossing radially the drilled gasket was measured using a helium mass spectrometer (ASM% 181 T2H Alcatel) for determining the radial leak rates. In order to measure the permeability *in plane* leak only, two latex films (12 mm external diameter, 5 mm internal diameter, 0.12 mm thickness)

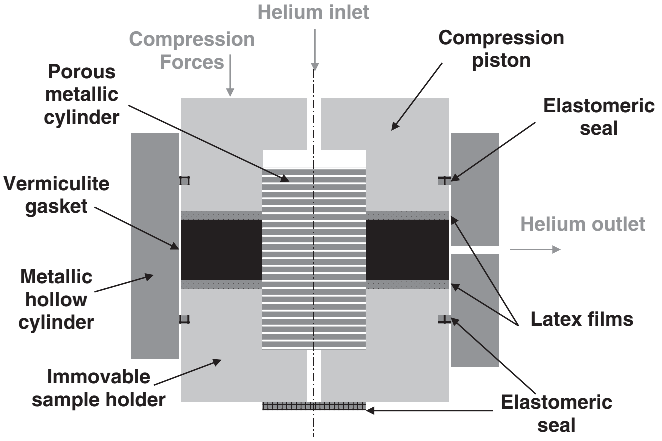

Fig. 1. Schematic section representation of the gasket holder setup for the measurement of the total radial and the *in-plane* leak rates.