PUBLICATION II

Effects of the first heat up procedure on mechanical properties of solid oxide fuel cell sealing materials

Journal of Power Sources. Elsevier. Vol. 284 (2015), 511–516.

Journal of Power Sources 284 (2015) 511–516

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Effects of the first heat up procedure on mechanical properties of solid oxide fuel cell sealing materials

Markus Rautanen*, Valtteri Pulkkinen, Johan Tallgren, Olli Himanen, Jari Kiviaho

VTT Technical Research Centre of Finland, Fuel Cells, P.O. Box 1000, Biologinkuja 5, Espoo FI-02044 VTT, Finland

HIGHLIGHTS

- Mechanical properties of glass, compressible, and hybrid SOFC seals were studied.
- Compressibility of the materials is presented at different temperatures.
- The effect of first heat up on mechanical properties of the materials is presented.
- Design guidelines are given for stack assembly and first heat up.

ARTICLE INFO

Article history:
Received 29 November 2014
Received in revised form
20 February 2015
Accepted 3 March 2015
Available online 5 March 2015

Keywords:
SOFC
Seal
Stack
Hybrid
Compression
Stress

ABSTRACT

SOFC stack seals need to be correctly dimensioned to achieve a gas tight stack with low electrical contact resistances. Mechanical properties of SOFC stack sealing materials are presented for three assembly and first heat up procedures: applying full compressive stress at room temperature before first heat up (1), applying no compressive stress before first heat up and applying the full compressive stress at operating temperature (2), applying partial compressive stress at room temperature and full compressive stress at operating temperature after first heat up (3). The behaviour of the glass seal (Schott GM31107) is not affected significantly by compressive force during heat up. Compressibility of both compressible sealing material (Thermiculite CL87) and hybrid sealing material (Thermiculite CL87LS) was found to be about 40% (between 0.1 and 0.9 MPa) at room temperature but only about 4% (between 0.1 and 0.9 MPa) at 700 °C. Therefore it is beneficial to carry out as much of the compression as possible at room temperature before first heat up. This allows for maximum amount of deformability in the sealing materials resulting in the highest ability to compensate for stack manufacturing and assembly tolerances, which is needed to realize a gas tight stack with low electrical contact resistances.

1. Introduction

One of the key challenges in solid oxide fuel cell stack development is achieving a robust mechanical design. SOFC stack consists usually of steel interconnect plates, cells and seals. The only component of these that can offer a significant amount of deformability is the seal, which needs to compensate for manufacturing and assembly tolerances of other components in a stack. Understanding mechanical properties of sealing materials is important as improper seal design can lead to poor electrical contact, gas leakages and cause additional mechanical stresses to the stack [1–4]. A stack designer needs to know the mechanical properties of the seals not only at room temperature or at operating temperature but throughout the whole operating region. Of special interest are the mechanical properties of materials during the first heat up, in which the stack is sealed, reduced and tested before shipping to customer.

The two most common groups of sealing materials used in SOFC stacks are glass seals and compressible seals from the mineral group called mica [5]. At least for the first group, mechanical properties depend not only of temperature but of heat treatment history due to phase changes such as crystallization of amorphous glass phases. Compressible seals from the mica group are usually used in a form of mica paper or other highly anisotropic forms [6]. Therefore sufficient experimental data of the chosen set of materials is a necessity for the stack designer. Literature data of the mechanical properties of SOFC sealing materials is usually not

* Corresponding author.
E-mail address: markus.rautanen@vtt.fi (M. Rautanen).

http://dx.doi.org/10.1016/j.jpowsour.2015.03.012
0378-7753/

sufficient to provide enough input for designing a stack. Properties of various glasses are often measured with hot stage microscopy, see e.g. Ref. [7]. While this is a simple and reliable method in determining mechanical changes in glass samples, it is very removed from the actual conditions inside a stack: there is no compressive force applied on the sample and there is only one (bottom) surface for the glass to wet, making the situation unrealistic. In the case of compressible sealing materials, literature data on the mechanical properties is rather focused on the mineralogical properties of mica-materials [6,8] and data related to designing SOFC stacks is scarce [9,10].

This article presents mechanical properties of three sealing materials: a compressible seal, glass seal and hybrid seal. The focus is on the first mechanical compression of stack after assembly and on the first heat up procedure. Three possible procedures for applying the compression to the stack were investigated:

1. applying full compressive stress at room temperature before first heat up,
2. applying no compressive stress before first heat up and applying the full compressive stress at operating temperature (700 °C) and
3. applying partial compressive stress at room temperature and full compressive stress at operating temperature (700 °C) after first heat up.

Compressibility data of these cases is presented and its significance to stack design and manufacturing process is discussed. Results and discussion are presented from SOFC point of view but it is equally applicable to solid oxide electrolysis (SOEC) stacks.

2. Experimental

2.1. Materials

Three sealing materials were chosen for this study: glass (Schott GM31107), compressible sealing material (Thermiculite CL87, Flexitallic Ltd) and hybrid sealing material (Thermiculite CL87LS, Flexitallic Ltd). The first material is a traditional glass sealing material manufactured by Schott. Viscosity of the glass at it's softening temperature of 649 °C is $10^{6.6}$ Pa and at 750 °C 10^5 Pa [7]. Based on previous studies, the glass has good bonding properties at 700 °C with both Crofer 22H steel and Thermiculite 866 sealing material [11]. The glass powder is cast into a tape of 250 μm green thickness.

The second material is a compressible sealing material based on chemically exfoliated vermiculite and steatite. This material is an offspring of the Thermiculite 866 range [12].

The third material is based on the same compressible core but includes a coating of Schott GM31107 glass and organic binders diminishing interfacial leaks and thus allows it to be used at very low compressive stress levels (<1 MPa). For more details on this material, see Refs. [9,13]. The amount of glass in the coating was 5 mg cm^{-2}. The density of the core material of Thermiculite CL87 and CL87LS was 0.85 g cm^{-3} and weight per unit area was 36 mg cm^{-2}. Before testing, the materials were stored in a constant temperature and humidity room (T = 22 °C, RH = 42%) as humidity might affect the compressibility of Thermiculite materials.

2.2. Test setup

A double push-rod mechanical dilatometer was used to measure material thicknesses in this study. Fig. 1 presents the basic principle of the device. A sample is inserted between the measurement rod and weight is clamped on the top of both rods. The thickness of the sample is read of a dial gauge mounted at the top of the push-rods.

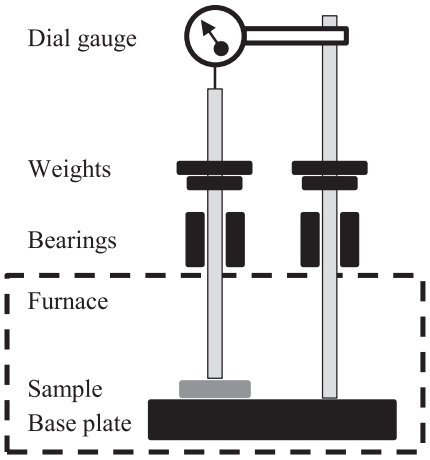

Fig. 1. Schematic of the used measurement setup.

The lower part of the assembly can be inserted in a dedicated furnace to control the temperature of the sample. The double push-rod design allows for the compensation of thermal expansion in the push-rods and therefore allowing for high accuracy. To test the accuracy of the measurement setup, calibration measurements were done at room temperature with 500 μm, 750 μm and 1000 μm precision strip steel plates. Results indicated a constant systematic error of 6 μm. The known, systematic error was reduced from actual measurements with seal materials. Accuracy of the device at elevated temperatures was studied with zero point deviation measurements where no sample material was present. The average zero point error was 0.5 μm and random uncertainty 0.9 μm (considered to be 2σ). Furthermore the accuracy of the device was studied by measuring thermal expansion of Crofer 22H plate and comparing the results against thermal expansion data provided by the manufacturer [14]. Fig. 2 shows the measured and calculated thicknesses of the Crofer 22H plate. Initial thickness of the plate was 1020 μm and the end value at 800 °C was 1029 μm. The measured values are in good agreement with the data provided by the manufacturer: average difference is 1.2 μm and random uncertainty 2.6 μm (2σ of residuals). Based on the above analysis, accuracy of the device is considered to better than ±10 μm at operating range of 0–700 °C.

2.3. Test cases

To simulate first compression and heat up treatments of stacks, three different procedures were tested for all materials:

1. applying full compressive stress (1 MPa) at room temperature before first heat up,
2. applying no compressive stress before first heat up and applying the full compressive stress (1 MPa) at operating temperature (700 °C) and
3. applying partial compressive stress (0.44 MPa) at room temperature and full compressive stress (1 MPa) at operating temperature (700 °C) after first heat up.

Applying full compressive force at room temperature (case 1) could be done during assembly process of a stack. However, applying virtually no compression at room temperature before first heat up might be necessary with initially thick green glass tapes if e.g. mechanical structure of the stack is such that it will deform under compressive stress. In such a case full compression can only be applied at operating temperature (case 2). A compromise

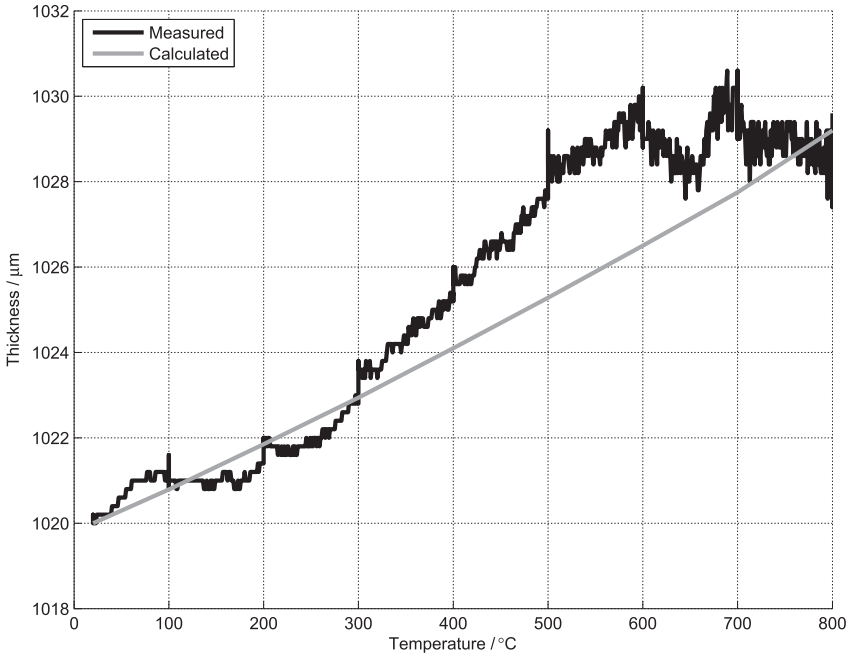

Fig. 2. Measured thickness of Crofer 22H plate (1020 µm initial thickness) as a function of temperature together with calculated thickness based on manufacturers datasheet.

between these two is the case 3 where partial compressive stress (0.44 MPa) is applied at room temperature and final compressive stress (1 MPa) at operating temperature.

3. Results and discussion

3.1. Glass seal

The three procedures for compression and first heat up were tested. Fig. 3 shows Schott GM31107 glass sealing material thickness as a function of temperature and time. The grey curve corresponds to heating under 0.44 MPa of compressive stress and the black curve to heating under no compressive stress. Heating rate was 60 °C/h and the shown temperature corresponds to furnace temperature. This means that the temperature of the sample lags behind the shown furnace temperature during heating, meaning it should be only considered as indicative until reaching steady state. It is noticed that there is only very little thickness change until about 570 °C. Above that temperature two distinct changes are noticed, the first at 570–615 °C and the second at 660–700 °C. Based on hot stage microscopy data [7], the first of these changes relates to binder burn out and sintering and the second change to softening and wetting of the surfaces. The final thickness of the glass was about 12 µm at 0.44 MPa. Further compression to 1.0 MPa

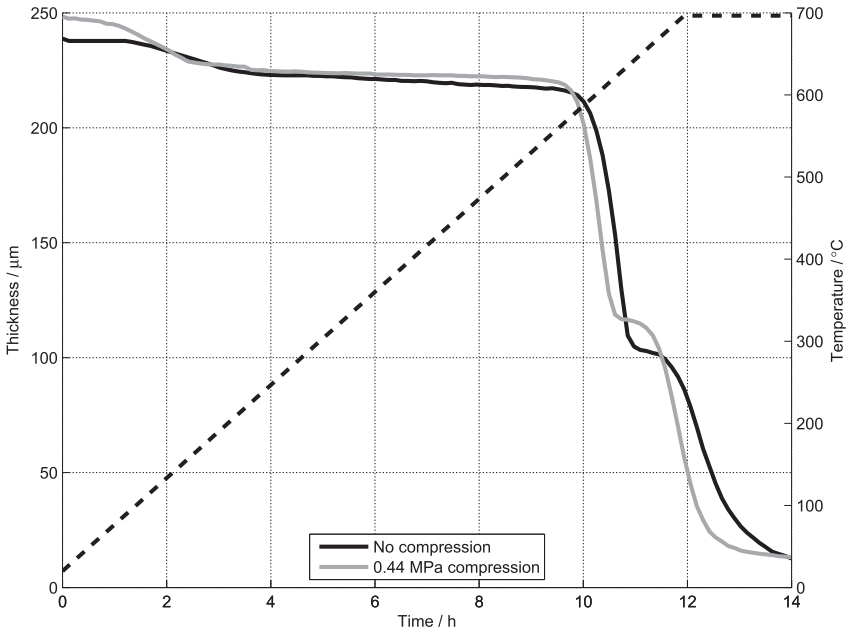

Fig. 3. Glass seal heated up at 0.44 MPa compressive stress.

at 700 °C did not reduce this thickness. The difference throughout the heating using 0.44 MPa of compressive stress and no stress at all is minimal.

Based on these results, behaviour of the Schott GM31107 glass does not depend greatly on compression procedure during first heat up. However, if a significant amount of compression is applied at room temperature where the glass tape is very thick compared to its final thickness, the stress distribution within a stack structure should be analysed to be sure that stresses are within acceptable limits.

3.2. Thermiculite CL87

Fig. 4 shows the effect of temperature on the compressibility of the seal. It can be noted that heating the material significantly reduces the compressibility: already at 200 °C the compressibility is the same as at 700 °C. If the compressive stress is applied at room temperature before first heat up, Thermiculite CL87 compresses about 42% between 0.1 and 0.9 MPa. If full compression to 1.0 MPa is applied after first heat up, the compressibility between 0.1 and 0.9 MPa is limited to 4%. The compressibility (slope of the thickness vs. stress curves) at 700 °C remains the same for both cases and is not affected by the pre-compression at room temperature. Most probably the loss of compression is related to drying of the sealing material and therefore it is likely that any heating above room temperature results in partial loss of compressibility. Based on these results the best practise would be to apply at least part of the compression already at room temperature. Fig. 5 shows the compressibility curves of Thermiculite CL87 in the three different heat up cases. It can be noticed that compressibility is very significantly affected by the application method of compressive stress.

These results indicate that with Thermiculite CL87 the preferred method of stack assembly should be to apply a major part of the compression already at room temperature as compression at operating temperature requires roughly ten times more stress to induce similar deformation in the sealing material. Applying compression at room temperature gives the sealing material the best chance to compensate for manufacturing and assembly tolerances leading to a gas tight stack with low electrical contact resistance.

3.3. Thermiculite CL87LS

Fig. 6 shows compressibility of Thermiculite CL87LS at different temperatures. It is noticeable that the initial thickness of the material (below 0.4 MPa) is higher at low temperatures than at operating temperature. This is due to the binder burn out, shrinkage and sintering of the coating layer which naturally only occurs during heating. The low-stress difference between measurements conducted at room temperature and at operating temperature is associated with the final thickness of the glass layer.

Fig. 7 shows compressibility curves of Thermiculite CL87LS corresponding to the three test cases. It can be noted that the general behaviour follows that of Thermiculite CL87 which is expected as the core material is the same. However, Thermiculite CL87LS is slightly thicker because of the coating. The thickness of the material is also reduced during heat up as binders evaporate from the coating and glass particles sinter. This is especially noticeable by looking at the sample that has been pre-compressed to 0.44 MPa at room temperature (grey dashed line). After pre-compression the same sample was heated to operating temperature and compressed 1.0 MPa (black dashed line). The thickness during heating has been reduced by around 10% (580 μm–520 μm).

These results indicate that also with Thermiculite CL87LS the preferred method should be to apply as much compression as possible already at room temperature to ensure maximum amount of deformability of the seal.

4. Conclusions

Compressibility of SOFC stack sealing materials was evaluated for three assembly and first heat up procedures. The behaviour of the glass seal (Schott GM31107) was not affected significantly by compressive force during heat up. The end thickness of the 250 μm

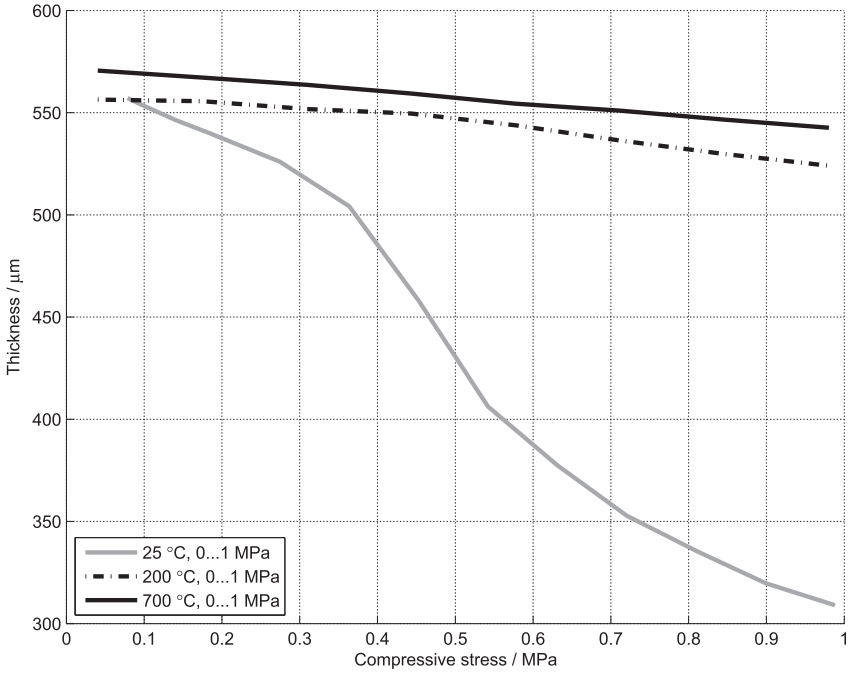

Fig. 4. Compressibility curves of CL87 at different temperatures.

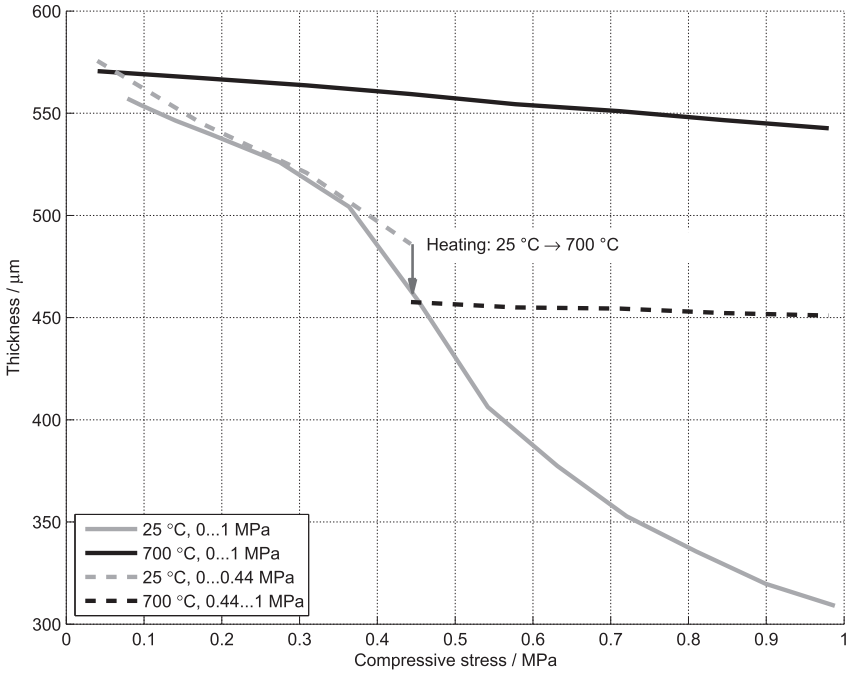

Fig. 5. Thermiculite CL 87 compressibility curves. Grey lines indicate compression at room temperature and black lines at operating temperature (700 °C). The grey dashed line represents pre-compression at room temperature and black dashed line the same sample after heat up.

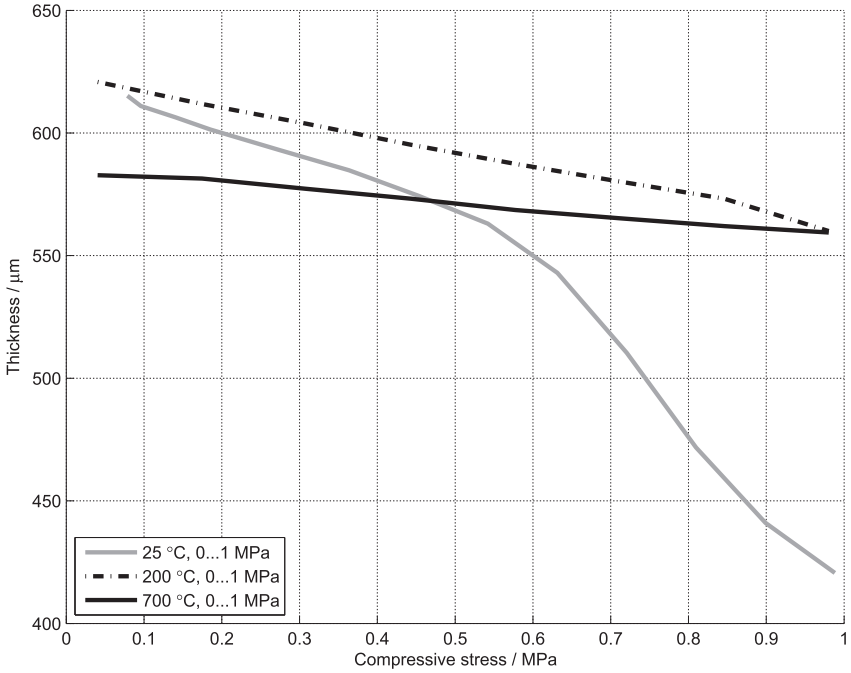

Fig. 6. Compressibility curves of CL87LS at different temperatures.

(green thickness) tape at 700 °C was about 12 µm independent of compressive stress (0–1 MPa). Compressibility of both Thermiculite CL87 and CL87LS materials was found to be around 40% between 0.1 and 0.9 MPa at room temperature, meaning these materials are well able to compensate for manufacturing or assembly tolerances in a stack. However, a significant amount of compressibility is lost when the material is heated: at 700 °C the compressibility is only around 4% between 0.1 and 0.9 MPa. Therefore it is very beneficial to carry out as much of the first compression as possible at room temperature before first heat up. This would allow for maximum amount of deformability in the sealing materials resulting in the highest ability to compensate for stack manufacturing and assembly tolerances leading to a gas tight stack with low electrical contact resistances. The provided methodology, data and guidelines should allow for a stack designer to optimize the mechanical design, first compression during assembly and first heat up procedure of the stack.

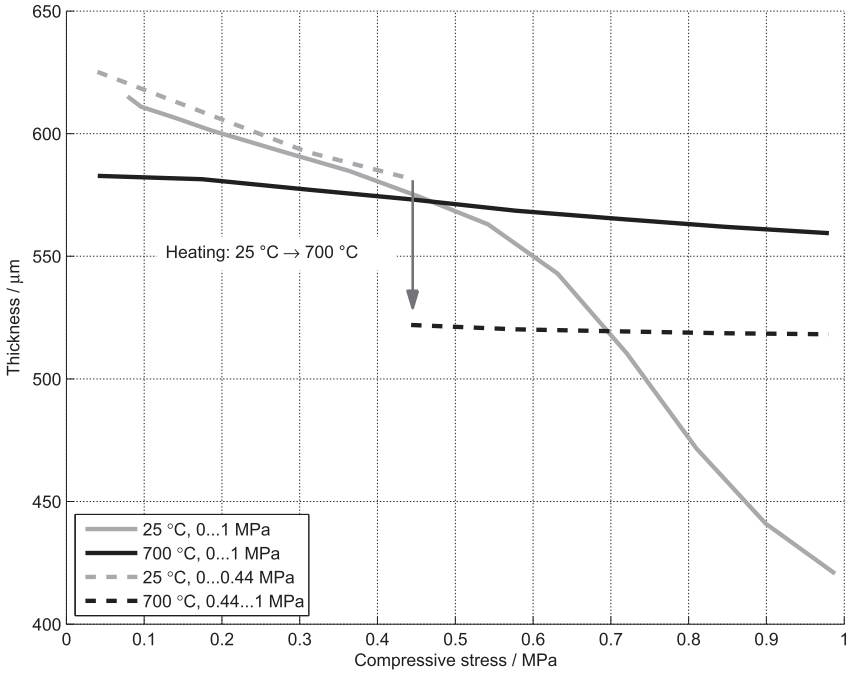

Fig. 7. Compressibility curves for Thermiculite CL 87LS. Grey lines indicate compression at room temperature and black lines at operating temperature (700 °C). The grey dashed line represents pre-compression at room temperature and black dashed line the same sample after heat up.

Acknowledgements

This research was supported by the Fuel Cells and Hydrogen Joint Undertaking under grant 621227 (NELLHI). Olivier Thomann, Kari Koskela and Juha Järvinen of VTT Technical Research Centre of Finland are acknowledged for useful discussions regarding this work.

References

[1] S. Gross, D. Federmann, J. Remmel, M. Pap, Reinforced composite sealants for solid oxide fuel cell applications, J. Power Sources 196 (2011) 7338–7342.
[2] L. Blum, S. Gross, J. Malzbender, U. Pabst, M. Peksen, R. Peter, I. Vinke, Investigation of solid oxide fuel cell sealing behaviour under stack relevant conditions at Forschungzentrum Jülich, J. Power Sources 196 (17) (2011) 7175–7181.
[3] A. Nakajo, F. Mueller, J. Brouwer, J. Van herle, D. Favrat, Mechanical reliability and durability of SOFC stacks. Part II: modelling of mechanical failures during ageing and cycling, Int. J. Hydrog. Energy 37 (11) (2012) 9269–9286.
[4] C.-K. Lin, L.-H. Huang, L.-K. Chiang, Y.-P. Chyou, Effects of clamping load on the thermal stress distribution in a planar SOFC with compressive sealing, ECS Trans. 25 (2) (2009) 349–358.
[5] J.W. Fergus, Sealants for solid oxide fuel cells, J. Power Sources 147 (1–2) (2005) 46–57.
[6] S. Habelitz, G. Carl, C. Rüssel, S. Thiel, U. Gerth, J.-D. Schnapp, A. Jordanov, H. Knake, Mechanical properties of oriented mica glass ceramic, J. Non-Cryst. Solids 220 (1997) 291–298.
[7] D. Gödeke, J. Besinger, Y. Pflügler, B. Ruedinger, New Glass Ceramic Sealants for SOFCs, ECS Trans. 25 (2) (2009) 1483–1490.
[8] S.P. Simner, J.W. Stevenson, Compressive mica seals for SOFC applications, J. Power Sources 102 (1–2) (2001) 310–316.
[9] J. Hoyes, M. Rautanen, SOFC sealing with Thermiculite 866 and Thermiculite 866 LS, ECS Trans. 57 (1) (2013) 2365–2374.
[10] M. Rautanen, O. Himanen, V. Saarinen, J. Kiviaho, Compression properties and leakage tests of mica-based seals for SOFC applications, Fuel Cells (2009) 753–759.
[11] M. Rautanen, O. Thomann, O. Himanen, J. Tallgren, J. Kiviaho, Glass coated compressible solid oxide fuel cell seals, J. Power Sources 247 (2014) 243–248.
[12] J. Hoyes, S. Bond, Gaskets for sealing solid oxide fuel cells, Seal. Technol. 2007 (8) (2007) 11–14.
[13] Flexitallic, "Thermiculite 866/866LS," Flexitallic Ltd, [Online]. Available: http://www.flexitallicsofc.com/downloads/Flexitallic_SOFC_thermiculite_866.pdf. [Accessed 28 01 2015].
[14] ThyssenKrupp. [Online]. Available: http://www.fcdic.com/ja/member/data/Crofer22H.pdf.