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Glass composite seals for SOFC application

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Abstract

Glass composite materials were investigated for use as a seal between Fe78Cr22 steel interconnects and cell components. Additions of MgO-filler to the sodium aluminosilicate (NAS) base glass increased the coefficient of thermal expansion of the composite to ∼12 ppm and provided a sufficient match between the components to allow for thermal cycling of the interfaces. The optimisation of composite seals with long-term compliancy showed promising results in terms of being able to control both the bonding strength and interface reactivity between metal and glass. The reactivity increased with temperature and protection of the surface by pre-oxidation did not alter the picture. Etching the metal surfaces in combination with application of Mn-, Co-, or Ni-oxide coatings reduced the metal–glass interactions and for the Ni- and Co-oxide coatings facilitated an excellent bond and gradual changing interface between the glass and metal.

Samples were tested in model experiments and performance tested in multi-cell stacks. Both pure NAS glass and NAS/MgO composite material developed gas tight sealing performance, when sealed at 950 °C and showed low, constant levels of leakage throughout multiple thermal cyclings after more than 5000 h run time in stack testing.

Keywords: Glass; Composite; Seal; Corrosion; Fuel cell

1. Introduction

Glass is a versatile material and has been widely used for sealing in the ongoing development of intermediate temperature solid oxide fuel cell technology where the physical and chemical properties of a glassy seal can be tailored to the other components, i.e. metallic interconnect and ceramic fuel cell, even though the coefficients of thermal expansion (CTE) usually must be in the range 11–13 ppm/K and higher than the CTE of most base glasses. Although high-expansion glasses are known, other demands, such as deformability at the sealing temperature and long-term stability of the seal, often limit the number of applicable glass systems.

Literature reports on glass and glass–ceramic compositions within the groups of alkali silicates, alkali aluminosilicates and alkaline earth aluminoborosilicate,[1–10] illustrating two equally viable sealing strategies. One route, which focus on composite seal materials from a compliant glass and a dispersed filler material with high CTE, e.g. MgO, have shown promise in terms of exact matching the CTE between the sealant and the seal surfaces, and at the same time attain suitable values of T_g and sufficient wetting of the surfaces. Further, it shows a high stability and a slow crystallisation behaviour.[5] Similar performance was recently reported also for metallic filler materials in alkali boron silicate glass.[11] The other route, using glass–ceramic materials with fast crystallisation behaviour and high final CTE[7–10] results in a solid bond, which ideally stays unaffected during the life-time of the stack.

The need for long-term compliancy through a slow crystallisation behaviour in the glass matrix mainly depends on the magnitude of thermally induced stress between the components, for instance as consequence of stack design and accuracy of the thermo-mechanical match between sealant and the neighbour stack components. Although successful in terms of thermo-mechanical performance, the corrosive action of the alkali aluminosilicates and alkaline earth aluminoborosilicate glasses on the interconnect[4,6,7] often limits the applicability in planar SOFC stacking, because corrosion causes destabilisation of the protective chromia scale on the interconnect, which can not be tolerated due to the small thickness of the component.

The present paper focuses on the optimisation of composite seals with long-term compliancy based on a sodium aluminosil-

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icate (NAS) glass ($T_g = 515\,^\circ C$) with MgO-filler. Exploratory studies on the mechanical and chemical interactions between such glassy seal materials and ferritic interconnect steels, Crofer 22APU and Fe22Cr-type test melts from Sandvik, generally showed promising results for a number of combinations. The aim is to understand and counteract the excessive corrosion through variations of the interface chemistry; for instance, by application of thin metal-oxide coatings to the metal part prior to sealing.

In earlier formulations of the seal composite,[4] partial dissolution of the MgO-filler into the NAS glass is minimised by using only larger MgO-grains, $d = 90–200\,\mu m$ because magnesium is expected to increase surface tension of the glass,[12] and dependent on concentration, increase viscosity.[13] However, as consequence of such partial dissolution an improved overall wetting and bonding behaviour is observed[6] even though other corrosive reactions at the glass-to-steel interfaces tends to complicate the analysis of bonding mechanisms. Therefore, fine-grained MgO-filler or filler material with bimodal grain size distributions was used in the present study to enhance the bonding capability of the glass matrix.

2. Experimental

The NAS glass was melted from analytical grade chemicals SiO_2, Al_2O_3 and Na_2CO_3 in an alumina crucible at 1650 °C for 2 h, crushed and re-melted in order to ensure homogeneity, reaching a final composition: Na_2O: 17.8 mol%, Al_2O_3: 9.4 mol%, SiO_2: 72.8 mol%. Finally, the glass was milled into fine powder, $d_{50} = 24\,\mu m$, which was combined with the coarse fraction of MgO powder, $d = 90–200\,\mu m$, into one type of glass composite with 45 vol.% filler ($CTE_{RT\text{-}800} = 12$ ppm/K) further uniaxially pressed into bars, partially sintered at 800 °C for 2 h and machined before used as thermo-mechanically matched seal in stack testing.

Other composites with 7 and 30 vol.% filler were made as thin films having dried thicknesses of $\sim 260\,\mu m$ by tape casting finer glass powder, $d_{50} = 5.5\,\mu m$, and finer MgO-filler material, $d < 10$ and $39\,\mu m$, respectively, suspended in an organic vehicle. The tapes were sandwiched between either interconnect materials or fuel cell support materials for seal testing.

Steel samples were machined to dimensions and, except for those with the 'as-received' and abraded surfaces, etched by HNO_3/HF-solution in an ultrasonic bath. All samples were then rinsed in ethanol and dried. Abraded metal surfaces were prepared by using SiC-paper (grit 1000). Pre-oxidation of metal surfaces was performed in air at 850 °C for 10 min in a preheated furnace.

Slurries for spray-coating the metal surfaces were prepared by ball milling metal-oxides (Co-, Ni-, Mn-oxide, respectively) suspended in an organic vehicle until an average particle size in the range 0.8–5 μm were obtained, after which they were applied to etched samples, having dried layer thicknesses in the range 5–7 μm.

Interconnect samples and thin film samples of seal composites were stacked in sequences and run simultaneously to expedite the screening process. The sandwiches were subjected to heat treatments at two different temperature levels (850, 950 °C) to evaluate the sealing performance, durability and reactivity between interconnects and glass composites at sealing temperatures of interest. A pressure of 120 kPa was applied to the samples and heating was performed at constant rate, 2.5 °C/min, until the soak temperature, which was then held for 160–170 h before cooling to room temperature at nominally 2.5 °C/min.

Performance of selected seals were tested in two short stack experiments, fuelled by hydrogen and either 3–4 vol.% or 20 vol.% water. One type of seal composite from the NAS glass with 45 vol.% coarse MgO-filler was tested in a three-cell stack. The stack was initialised at 950 °C and thermally cycled after 1620 h service at 750 °C. The stack had external gas-manifolding, also sealed with the same composite material, and ran for 3700 h in total. Each stack element, shown schematically in Fig. 1, comprises the SOFC-cell sandwiched between a set of current collectors and interconnect plates of Crofer 22APU. Another type of seal from the same NAS glass without filler was tested in a single-cell stack test. Here, thin films of the sealant was applied to both sides of a metallic spacer before being mounted in the stack assembly similarly to the seals used in the three-cell stack, cf. Fig. 1. After the initial activation of the single-cell stack assembly at 950 °C, the temperature was maintained at 750 °C for about 2100 h until the first complete thermal cycle, performed at heating and cooling rates of 3 °C/min. This was repeated five times over the last 1000 h of stack operation prior to the termination of the test, cf. Table 1. At the conclusion of a thermal cycle, the leak rate was calculated to determine if any catastrophic fracturing had occurred within the glass seals or electrolyte. Leak rate calculations were based on the response from oxygen monitors in the gas compartment on both inlet and outlet of the stack together with the hydrogen mass

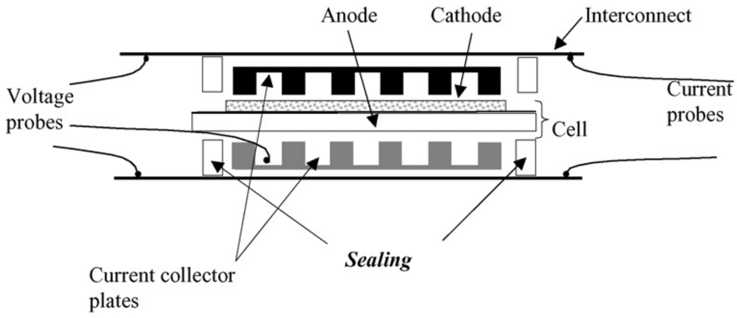

Fig. 1. Stacking components schematically.

Table 1
Calculated leak rates after initialisation and following six thermal cycles

Time (h)	Equivalent leak current (mA/cm^2)
0	27
2160	21
5000	26
5100	24
5200	18
5250	23
5400	18

flow, which were compared to the current density through the stack.

Particle sizes were measured on a Beckman Coulter LS particle size analyser. Coefficients of thermal expansion (CTE) were measured in a Netzsch DIL 402C ramping at 2 °C/min. XRD analysis was done in a STOE STADIP diffractometer (Cu-α) 2Θ from 10° to 80°. Microscopy and element analysis was done on polished cross-sections of samples in a JEOL JSM 5310 LV microscope equipped with energy dispersive X-ray detector.

3. Results and discussion

Good adhesion between the glass composite and interconnect steel is exemplified in Fig. 2, showing the NAS/MgO thin film composite against pre-oxidised surfaces of Sandvik test melt after testing at 850 and 950 °C. The images from back-scattered electrons enhance the distribution of elements as also seen from elemental analysis by EDX spectroscopy. The light grey and whitish deposits on the MgO-particles in the seal composites were dominated by chromium oxides with a lesser amount (<15 at.%) of MgO, often with traces of oxides from the glass (Si, Al) or iron oxides from the metal. These deposits were always concentrated on the side of the MgO-grains that faced the metal–glass interface and looked as if they were formed by condensation of diffusing substances. The formation of sodium chromate (Na_2CrO_4), a relatively low-melting compound ($M_p = 792\,°C$),[14] was expected to destabilise the protective chromia scale on the interconnect, but sodium and chromium oxides seemed never to co-exist in the glass–steel interface region. The glassy transition zone between the innermost row of MgO-grains and the steel interface, cf. Figs. 2 and 3, was gradually enriched in chromium when moving from the areas of the pristine glass towards the metal surface and at the same time gradually depleted in sodium, often to a degree where sodium was absent close to the metal surface. The thickness of the transition zone varied for the present set of experiments between 2 and 80 μm as a function of both glass composite composition and the metal surface treatment, and it generally increased with the sealing temperature. The immediate hypothesis therefore is that sodium evaporated as a consequence of the oxidation of metallic chromium, cf. Eq. (1), and escaped through the open porosity before the glass softened and closed off the interconnect surface from the atmosphere. Chromium, most likely was transported to the MgO grains via gaseous Cr^{VI}-species. Eq. (1) only describes the overall reaction leading to the chromia, which was identified at the interfaces:

$$Na_2O(sol) + O_2(g) + 2Cr(s) \Leftrightarrow Cr_2O_3(s) + 2Na(l/g) \quad (1)$$

Surplus of oxygen would yield different products:

$$Na_2O(sol) + 1.5O_2(g) + Cr(s) \Leftrightarrow Na_2CrO_4(s/l) \quad (2)$$

Sodium chromate is stable in air to only 974 °C and readily decomposes at 950 °C if the oxygen partial pressure is reduced by less than 5%,[15] which again reflects the volatility of sodium oxide under reducing conditions. Depletion of sodium from the glass in the interface was expected to cause poorer wetting and adhesion due to the increasing viscosity and tendency to primary crystallisation in the remanent glass. In contrast, the glass at the interface often looked vittreous and had good wettability. It may be explained by the dissolution of magnesium from the filler into sodium-depleted (Na)–Al–Si–O glass, which is reported[16] to dramatically change the temperature sensitivity of the glass viscosity dependence.

Fig. 3 shows micrographs of fairly good bonding between NAS and MgO thin film glass composite with 30 vol.% MgO-filler and 'as received' surfaces of Crofer 22APU. The narrow flaw running between the glass and the steel is typical

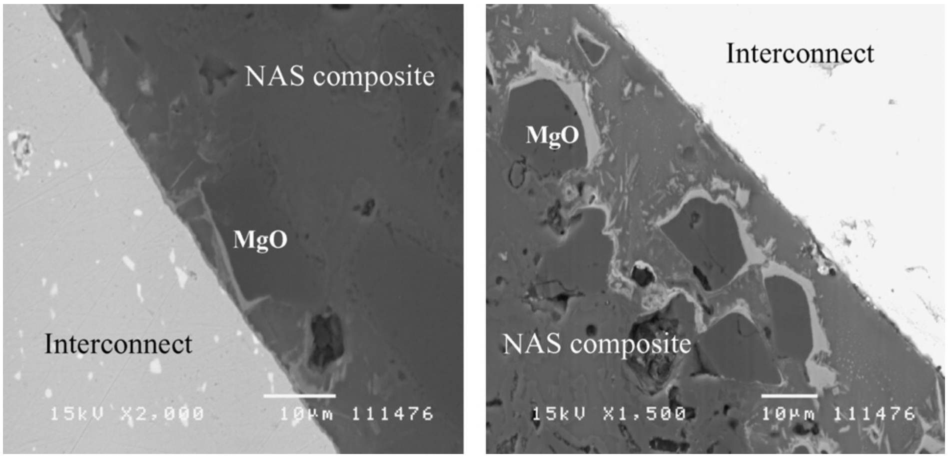

Fig. 2. Interface between pre-oxidised surfaces of Sandvik test melt, which is a chromia-forming type of steel and thin film NAS glass composite with 30 vol.% MgO-filler after 170 h at 850 °C (left) and 950 °C (right). Micrographs from back-scattered electron images on polished cross-sections.

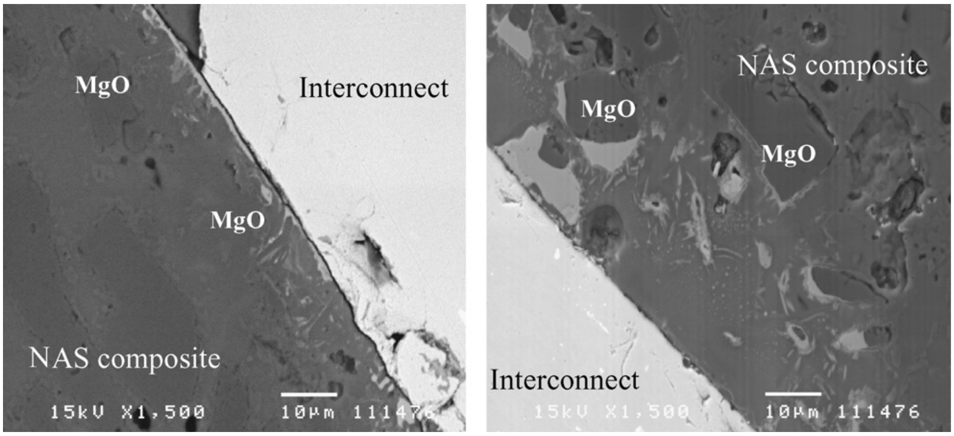

Fig. 3. Interface between Crofer 22APU (as received) and thin film NAS glass composite with 30 vol.% MgO-filler after 170 h at 850 °C (left) and 950 °C (right). Micrographs from back-scattered electron images on polished cross-sections.

for NAS–Crofer interfaces, and differs from the often flawless interfaces seen on the NAS–Sandvik interfaces. Crofer 22APU released significantly higher amounts of manganese, both into the oxide scale on the metal surface and into the glass next to the interfaces. A possible detrimental action of the manganese at the interphase is still not clear, but may be attributed to a higher susceptibility to reduction in the glass phase leading to a destabilisation of the glass network. Additional weakening of the interface is expected from corrosion of the grain boundaries in the surface layers on the Crofer 22APU, as indicated by the grains that seemed to be missing after sample preparation, cf. Fig. 3.

The performance test of the NAS composite material with 45 vol.% coarse MgO-filler sealing the three-cell stack test showed increased performance over the first 350 h run time, cf. Fig. 4, where both the cross-over leak and the bypass leaks decreased. Cross-over leak relates to the sealing between anode and cathode compartments, whereas bypass leak relates to leaks from the anode-inlet compartment to the environment, which was all sealed with the same glass composite material. Right at the conclusion of the thermal cycling at 1620 h the bypass leak increased significantly but then decreased over a shorter period almost to the previous level, whereas the cross-over leak gradually increased over 700 h before it decreased rapidly and stayed constant throughout the rest of the test. This self-healing behaviour has been ascribed to the compliancy of the NAS base glass, where partial dissolution of MgO-filler is expected to suppress primary crystallisation.[13] The glass bonded excellently to the fuel cell and bonded very well to the interconnect (Crofer 22APU) on both anode and cathode faces. However, severe corrosion was observed at the three-phase-boundary between interconnect, glass and cathode air, shown in Fig. 5 (left), where destabilisation of the protective chromia-layer lead to catastrophic oxidation. It is believed that the corrosion mechanism involved formation of sodium chromate; cf. Eq. (2), but only

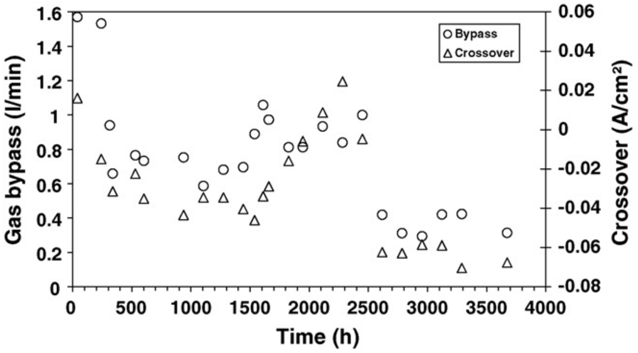

Fig. 4. Results from leak testing a three-cell stack throughout 3700 h of service, cycled thermally at 1620 h. Negative numbers for the cross-over leak indicates the level of accuracy. Fuel composition and current load changed at 2600 h.

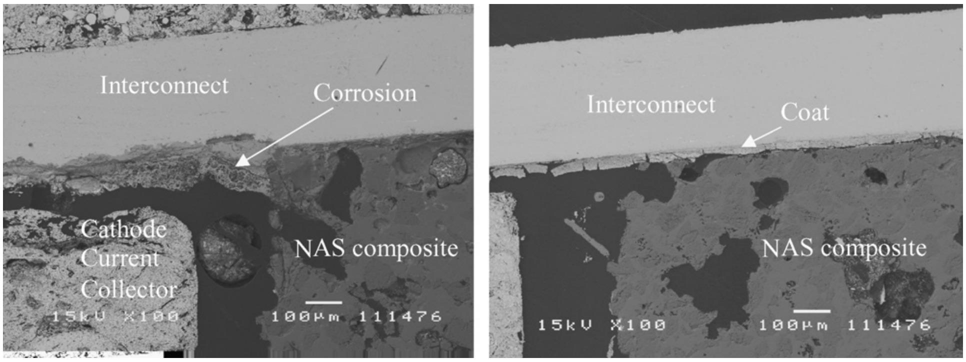

Fig. 5. Corrosion between cathode side air, CTE-matched NAS glass composite (45 vol.% MgO-filler) and Crofer 22APU interconnect steel after 3700 h at 750 °C as a function of either no metal-oxide coat on the steel surface (left) or a cobaltite-based coat (right).

Table 2
Qualitative assessment of the bonding behaviour between NAS and MgO glass composites and Crofer 22APU with different surface coatings and oxide layers

Crofer 22APU samples	NAS glass composite	850 °C/170 h		950 °C/170 h	
		Adh.	$d_{(\text{zone})}$ (μm)	Adh.	$d_{(\text{zone})}$ (μm)
Etched (HF/HNO$_3$)	30 vol.% MgO	−	16	0	80
Abraded	30 vol.% MgO	+	15	++	25
As received	30 vol.% MgO	+	10	0	27
Pre-oxidised (850 °C/10 min)	30 vol.% MgO	+	12	−	27
Etched + 5 μm NiO coat	30 vol.% MgO			++	25
Etched + 5 μm NiO coat	7 vol.% MgO			++	2
Etched + 5 μm Co$_3$O$_4$ coat	30 vol.% MgO			+++	15
Etched + 5 μm Co$_3$O$_4$ coat	7 vol.% MgO			++	2
Etched + 5 μm Mn$_3$O$_4$ coat	30 vol.% MgO			−	6
Etched + 5 μm Mn$_3$O$_4$ coat	7 vol.% MgO			0	5

Five levels were assigned to adhesion (Adh.): excellent (+++), good (++), fair (+), poor (−) and none (0) and listed together with the average width of the chromium–sodium-diffusion zone ($d_{(\text{zone})}$).

traces of sodium was found in the Fe–Cr-dominated oxide layer. Fig. 5 (right) shows an identical interface from the same stack, where the contact coating, which was applied to the metal surface before assembly, prevented the interface corrosion.

The performance of the thin film NAS glass sealing without MgO-filler, which may be considered a worst-case scenario, was evaluated by the results shown in Table 1. The leak rate was determined at the start of the test to be ~27 mA/cm^2, in terms of an equivalent electrical current loss. The nominal leak current decreased only little with subsequent aging, and as the experimental error in determining the values was typically found to be about ±5 mA/cm^2, the change on subsequent thermal cycling of the glass seals appears statistically insignificant. The microstructure of the seals was evaluated after testing and showed extensive primary crystallisation, which was assumed to be the Na–Al–Si-oxides, Albite and Nepheline according to the results from concurrent monitoring principal crystallisation in the composite by XRD. The bonding between glass and the cell was excellent and fair to both anode and cathode faces of the interconnect (Crofer 22APU) although the central parts of the sealing generally held a number of larger pores, most likely stemming from the initial porosity in the unfired glass tape.

The excellent performance of the thin film NAS glass sealing was surprising, bearing in mind that the CTE-mismatch (RT-750 °C) between the interconnect and the glass is 2.2 ppm/K and, at the same time, very promising for the technological potential of such seal design, provided the seal bonding and microstructure is further optimised. As shown above, addition of MgO-filler greatly enhanced the NAS glass seal performance, but did not solve completely problems with sodium depletion of the interface region. The application of a metal-oxide coat between the glass and the interconnect, cf. Fig. 5, effectively prevented the glass and metal interaction. Combining these experiences initiated an investigation of combinations between surface modification of the interconnect and additions of the MgO-filler at two levels of concentration and grain size (reactivity). The interconnect surface modifications included cleaning, pre-oxidation or coating with metal-oxides, which were selected from the group of transition metals, primarily among lighter elements known to facilitate good bonding between glass and metal.[17]

A clear difference in the metal reactivity was observed between etched and non-etched surfaces, cf. Table 2, but no significant differences were observed between abraded and slightly oxidised surfaces. The latter group probably appeared uniformly pre-oxidised after the heat-up sequence before the glass started to flow and exclude the air from reaching the metal surface. Etching, in contrast, activates the surface differently and particularly for the Crofer 22APU, where dissolution of grain boundaries were apparently visible in a light optical microscope after etching. When etching was combined with application of a thin coat of either nickel, manganese or cobalt oxide the reaction between NAS glass and metal is significantly suppressed, cf. Table 2, and in the case of nickel or cobalt oxide a strong and gradually changing interface is formed, as shown in Fig. 6. The sprayed-on

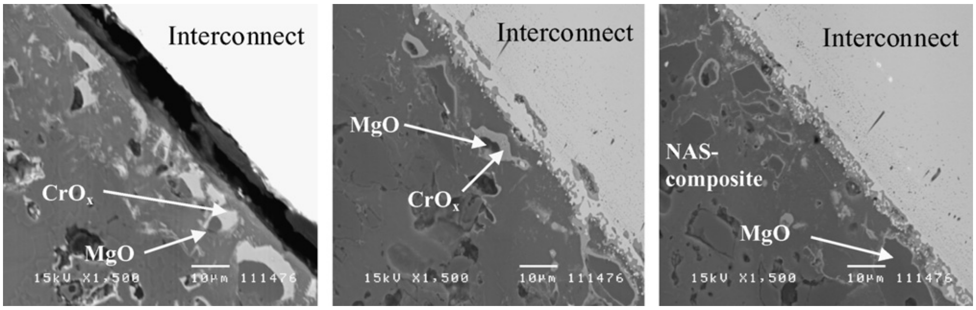

Fig. 6. Corrosion between thin film NAS glass composite (30 vol.% MgO-filler) and Crofer 22APU interconnect steel after 170 h at 950 °C as a function of surface coating. Left: etched; middle: etched + 5 μm Co$_3$O$_4$; right: etched + 5 μm NiO.

metal-oxides reacted with the chromium and formed an intermediate layer of mixed oxides, which prevented the reaction between chromium and sodium in the glass. The affinity between the metal-oxide and chromium decreased in the order: Mn, Co, Ni, if evaluated by the width of the reaction zone.

In order to evaluate the impact from the fine fraction of the MgO-filler on the resultant glass behaviour, both the average grain size and the amount were reduced in thin film glass composites (7 vol.% MgO, $d < 10\,\mu\text{m}$), which were applied to metal-oxide coated samples. In this case, the CTE of the glass composite no longer matched that of the interconnect, which became apparent through flaws in the glass composite after cooling to room temperature. The filler particles almost dissolved in the glass matrix and gave a fairly homogeneous structure with 10–15 mol% MgO in the glass as determined by EDS. The interface zone depleted in sodium was reduced to a few microns, cf. Table 2, and showed the strongest suppression of the reaction between chromium and sodium among all samples. Further, a very intimate contact between the innermost glass and the metal surfaces looked promising for future optimisation of the seal-interconnect behaviour.

4. Conclusion

The optimisation of composite seals with long-term compliancy based on the sodium aluminosilicate (NAS) glass with MgO-filler showed promising results in terms of being able to control both the bonding strength and interface reactivity between metal and glass. The reactivity in the interface region increased with temperature and protection of the metal surface by pre-oxidation did not alter the picture. Etching the metal surfaces in combination with application of Mn-, Co-, or Ni-oxide coatings reduced the metal–glass interactions and for the Ni- and Co-oxide coatings facilitated an excellent bond and gradual changing interface between the glass and metal. Reducing the average grain size and amount of MgO-filler further reduced the detrimental sodium depletion of the glass in the interface zone.

Both pure NAS glass applied as thin film sealings and NAS/MgO composite material applied as CTE-matched seal components developed gas tight sealing performance, when sealed at 950 °C. The NAS/MgO composite material showed self-healing properties after thermal cycling. The thin film sealing showed constant levels of leakage even after multiple thermal cycling after more than 5000 h run time in stack testing.

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