Ceramics for Energy Conversion, Storage, and Distribution Systems
Ceramics for Energy Conversion, Storage, and Distribution Systems

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Preface

The global challenges we face require innovative thinking and sustainable technology to meet increased demands for energy, clean water, and infrastructure. Research of materials—specifically, ceramic materials—continues to provide solutions to everyday challenges such as environmental protection, energy supply and generation, and healthcare. The 11th International Symposium on Ceramic Materials and Components for Energy and Environmental Applications (11th CMCEE), held June 14-19, 2015 at the Hyatt Regency Vancouver in Vancouver, B.C., Canada, identified key challenges and opportunities for ceramic technologies to create sustainable development.

This Ceramic Transactions volume contains papers submitted from the following six symposia held in Track 1: Ceramics for Energy Conversion, Storage, and Distribution Systems:

- High-Temperature Fuel Cells and Electrolysis
- Ceramic-Related Materials, Devices, and Processing for Heat-to-Electricity Direct Conversion
- Material Science and Technologies for Advanced Nuclear Fission and Fusion Energy
- Advanced Batteries and Supercapacitors for Energy Storage Applications
- Materials for Solar Thermal Energy Conversion and Storage
- High-Temperature Superconductors: Materials, Technologies, and Systems

After a peer-review process, 25 papers were accepted for inclusion in this proceedings volume. The editors wish to extend their gratitude and appreciation to all the symposium co-organizers for their help and support, to all the authors for their cooperation and contributions, to all the participants and session chairs for their time and efforts, and to all the reviewers for their valuable comments and suggestions. We also acknowledge the skillful organization and leadership of the meeting chairs, Mrityunjay Singh, Tatsuki Ohji, and Alexander Michaelis.

We hope that this proceedings will serve as a useful resource for the researchers
and technologists in the field of energy conversion, storage, and distribution systems.

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High-Temperature Fuel Cells and Electrolysis
EFFECT OF ADDITIVES ON SELF-HEALING OF PLASMA SPRAYED CERAMIC COATINGS

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ABSTRACT

MgAl₂O₄ coatings, used for electrical insulation along the metallic seals in high temperature fuel cell stacks, tend to fail prematurely due to generated stresses during on-off thermal cycles. To enhance stress bearing capability and the durability of these coatings, self-healing was investigated by introducing additives consisting of SiC as primary additive along with a secondary additive material. Secondary additives were one of the following compounds: BaO, CaO, ZnO, Y₂O₃, Al₂O₃, La₂O₃, TiO₂, GeO₂, Ce₀.9Gd₀.1O₁.95 (GDC) or Ta₂O₅. Crack healing can be attained due to reaction between SiC, secondary additive and oxygen that was transported to the additive due to a crack. Such reaction would be associated to a phase formation in the additive material linked with mass and volume increase assisting in closure of the advancing crack. Using TGA/DSC reaction temperatures and mass gains of SiC with or without secondary additives were identified. SiC+Y₂O₃ and SiC+ZnO were opted as promising additive materials. 20 wt% (SiC+Y₂O₃) containing MgAl₂O₄ coatings were produced by plasma spraying. In these developed coatings, healing was demonstrated after heat treatment at 1050°C in air for 10 hour. Defect healing in spinel coating with SiC+ZnO is under investigation.

INTRODUCTION

Defects in the sealing in high temperature solid oxide fuel cells (SOFC) has been reported as the foremost cause of failure in the fuel cell stacks¹,². The sealing, traditionally made of glass or glass-ceramic composites, ensures flow of fuel gas and air in designated compartments of SOFC stack. A leakage across the seal leads to catastrophic loss in cell potential and power output. Glass-based seals exhibit limited reliability which suffers further when the stack should undergo thermal transients such as during intermittent operation. In our earlier work³, an alternative approach was proposed in which Ag-based filler material is used for sealing of two consecutive cells. Despite mismatch of coefficient of thermal expansion (CTE) between filler alloy and neighboring components of stack, the high ductility and creep of the filler alloy compensate for stresses. However, as the filler alloy is electronically conductive, short circuiting between the cells is avoided by introducing an Mg-spinel (MgAl₂O₄) insulating coating in between. The spinel deposit is produced by plasma spraying. The schematic of sealing the approach is given in Figure 1. In spite of enhanced reliability compared to glass-based seals, the coating-braze based seals suffer from defects and cracks in the coating. These defects, associated to the manufacturing process or arise due to thermal cycling, give site for further crack nucleation and propagation, decrease the elastic modulus, yield strength and fracture energy of the coatings. At elevated temperatures crack initiation and propagation mechanism changes and failure may occur at the featureless zones, as suggested by Lawrie and Rawlings⁴. Overall, the increase in temperature from room temperature to 800°C caused a 23–30% reduction in flexural strength of bulk 8YSZ. Ansar et al⁵ have reported that the elastic modulus of plasma sprayed 8YSZ reduces from 35±2 GPa at room temperature (instead of 120 GPa for bulk material) to 16±1 GPa at 800°C. The decrease in elastic properties of such a coating was almost twice to bulk material and this was associated to the intrinsic elastic modulus of the YSZ but also to the structure of the splat boundaries.
Figure 1: Schematic of the SOFC stack sealing based on active braze and insulating coating.

Catastrophic failure in these insulation layers is a major limiting factor constraining the use of fuel cell in automotive applications. One approach to address this shortcoming consists of incorporating crack healing capabilities, which can offer improved reliability and service time of ceramic components. Though reported already in 1970’s\textsuperscript{6, 7}, this approach has limited work attributed to it to this day. Most studied self-healing ceramics are oxide ceramic matrix composites (CMCs) having 15 to 20 wt\% of well distributed SiC particles such as Al\textsubscript{2}O\textsubscript{3}/SiC\textsuperscript{8, 9} and mullite/SiC\textsuperscript{10, 11}. It was established that in SiC containing ceramic composites the healing occurs due to oxidation reaction, associated with volume expansion of new phases into the defects\textsuperscript{12}:

\[
\text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2 \ (\text{CO})
\]

(1)

Other studies suggested healing can be improved by promoting vitreous phase formation by using SiC+Y\textsubscript{2}O\textsubscript{3}\textsuperscript{13}:

\[
2\text{SiC} + \text{Y}_2\text{O}_3 + 4\text{O}_2 \rightarrow \text{Y}_2\text{Si}_3\text{O}_7 + 2\text{CO}_2 \ (\text{CO})
\]

(2)

As a result, cracks up to 100 \(\mu\)m were fully healed and the bending strength was increased by several folds.

Self-healing was also developed in other systems including ZrO\textsubscript{2}/SiC by thermal decomposition transformation to ZrSiO\textsubscript{4} and carbon black mixture\textsuperscript{14}. Additionally, crack healing ability was investigated in non-oxide ceramics such as Si\textsubscript{3}N\textsubscript{4} by introducing SiC\textsuperscript{15, 16}. In all materials presence of oxidizing environment is mandatory for a healing mechanism to occur and in most cases the minimum temperature at which full crack healing takes place has been reported at above 1000\degree C\textsuperscript{8-16}.

Incorporation of a material that can heal the defects in insulating ceramic layer in SOFC at elevated temperatures can significantly improve the stress bearing capability and fracture strength of these coatings. Insulating spinel coatings are primarily exposed to oxidizing environment which makes it realistic to achieve a crack healing mechanism. However the potential of healing capability can be best utilized if the reaction can be achieved at operating temperature of fuel cells which is around 800\degree C. The potential of such an approach is investigated in this paper. A range of potential self-healing additives consisting of primarily SiC along with secondary additives, BaO, CaO, ZnO, Y\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, La\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, GeO\textsubscript{2}, Ce\textsubscript{0.9}Gd\textsubscript{0.1}O\textsubscript{1.95} (GDC) or TiO\textsubscript{2} were tested and reported. Self-healing was demonstrated in Mg-spinel plasma sprayed insulating coatings using SiC+Y\textsubscript{2}O\textsubscript{3} as reference additive particles at 1050\degree C. It was suggested that addition of other tested additive compounds with SiC+Y\textsubscript{2}O\textsubscript{3} can effectively reduce reaction temperature well below 1000\degree C and in-operando healing can be potentially attained.
Effect of Additives on Self-Healing of Plasma Sprayed Ceramic Coatings

EXPERIMENTAL PROCEDURE
Self-healing additives

SiC and the secondary additive powders studied in this work are listed in Table 1. SiC with two different particle sizes were investigated submicron sized with d50 of 0.65 µm and nano sized with d50 of 50-60 nm. SiC and additive materials were mixed in molar ratio using an agate mortar and pestle. In order to understand the reaction mechanism of the mixed particles and to select the healing additives, Thermal gravimetric analysis (TGA)/ Differential scanning calorimetry (DSC), X-ray diffraction and Raman spectrometry have been performed. Reaction temperatures were defined by the commencement of weight gain (associated with volume expansion) on TGA data of the additive mixtures.

Table 1: List of the powder samples.

<table>
<thead>
<tr>
<th>material</th>
<th>particle size</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC (submicron)</td>
<td>650 nm</td>
<td>Iolite</td>
</tr>
<tr>
<td>SiC (nano)</td>
<td>50-60 nm</td>
<td>Iolite</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1-2 µm</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>CaO</td>
<td>&lt;160 nm</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1-2 µm</td>
<td>Merck</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;100 nm</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>GeO₂</td>
<td>1-2 µm</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>30-50 nm</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>BaO</td>
<td>1-2 µm</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Li₂O₃</td>
<td>1-2 µm</td>
<td>Fluka</td>
</tr>
<tr>
<td>GDC (GDC10)</td>
<td>1-3 µm</td>
<td>fuelcellmaterials</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>&lt;20µm</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

The TGA measurements were conducted in parallel with the DSC measurements using the STA 449C Jupiter® from Netzsch (D). The samples were tested in Pt-Rh crucibles from room temperature to 1200 °C (except for SiC+Ta₂O₅~1100 °C) with a constant heating rate of 5ºK/min. Synthetic air (O₂:N₂=20:80) and argon (Argon 5.0) at a flow rate of 30 ml/min were used as reaction and protection gases, respectively.

The mixed powders were analyzed by X-ray diffraction before and after the TGA/DSC measurements. The measurements were conducted using D8 Discover GADDS, equipped with a VANTEC-2000 area detector from Bruker AXS. A tuned monochromatic and collimated X-ray beam (Cu-Kα) was used.

For selected additive mixtures, Raman spectroscopy was conducted with a confocal Raman microscope (LabRam 800, Horiba Jobin Yvon). A green laser line (wavelength= 532 nm) was used for excitation. Mixed powders have been annealed in ambient air for 1, 5 and 10 hrs for Raman measurements.

Coating Fabrication and Characterization

MgAl₂O₄ and MgAl₂O₄ with SiC+Y₂O₃ were sprayed using air plasma spraying (APS) with a Triplex Pro 210 gun (Oerlikon Metco, Switzerland). 70±6 µm thick coatings were produced on Fe-Cr substrates from Thyssen group, Germany. In coated samples cracks were induced and were then annealed for different temperatures and times to investigate healing by microscopy. The
coating samples were also used for electrical conductivity measurements. For conductivity measurements, coatings were air brazed using filler alloy with a counter plate of 50x50 mm² Fe-Cr plate. The procedure is explained elsewhere. Four probe dc measurements were conducted as function of temperature. In addition, free-standing 1 mm thick coatings were prepared for dilatometry. For this purpose, coatings were sprayed on 7 mm x 44 mm plain carbon steel substrates followed by substrate dissolution by acid treatment in dilute sulfuric acid solution (1N) and applying dc voltage between the substrate and a counter metal electrode of 1.0-1.1 V. Self-healing in MgAl₂O₃ with SiC+ZnO are under investigation.

RESULTS AND DISCUSSION

Self-healing additives

Figure 2 (a) illustrates the TGA/DSC data of SiC with both particle sizes used in this work. In the DSC curve of nano-SiC, a broad depression is observed up to 900 °C. Such a behavior of nano SiC has been reported as oxygen adsorption on the surface. This was corroborated by the absence of this depression in the DSC curve in Ar atmosphere as shown in the figure 2(a). Corresponding weight gain due to oxygen adsorption on nano-SiC powder was less than 1%. Sub-micron SiC powder did not show this effect because of its lower specific surface area. Regardless of SiC particle size, an exothermic reaction above 900°C and an increase in its weight can be attributed to SiC oxidation. The oxidation is an exothermic reaction (heat value=943 kJ) which is described by equation (1).

Both micro and nano sized SiC was mixed Y₂O₃ and the TGA/DSC curves are given in Figure 2(b). In the case of SiC+Y₂O₃ powder mixture, a decrease in the mass up to 600°C is attributed to the evaporation of adsorbed water molecules from the Y₂O₃ surface owning to high surface area of nano-sized Y₂O₃. Such desorption in nano-sized Y₂O₃ was as previously also reported by Kuroda et al. Despite of the difference in DSC curves due to difference in SiC grain size at lower temperature zone (due to oxygen adsorption with nano-SiC), the data relevant to reaction zone appear independent of SiC particle size. As it is safe to say that there was negligible observable effect of particle size of SiC powders and as it does not influence TGA profile of the mixture significantly, the SiC particle size will not be discussed hereafter.

In Fig. 3, TGA/DSC curves of SiC+Al₂O₃, SiC+TiO, SiC+GDC and SiC+Ta₂O₅ are given. Both TGA and DSC are qualitatively similar to those of SiC. The results demonstrate that these additives have limited influence on promoting SiC oxidation or reaction formation.

The DSC data for SiC+CaO and SiC+BaO show an endothermic peak at the temperature where remarkable weight loss is observed and several exothermic peaks at higher temperatures (Fig. 4 (a)). The endothermic peak can be attributed to desorption of water molecules which have been adsorbed on the powder surface or contained in the powder as hydrates. The results demonstrate that those two samples have high reactivity at high temperatures and very hygroscopic in air. A similar characteristic, a small endothermic peak and remarkable weight loss, is also observed for SiC+La₂O₃ (Fig. 4 (a)). The TGA/DSC profile of SiC+GeO₂ shows a similar behavior as those in Fig. 3, however, a small endothermic peak is observed at 1110 °C which is followed by a remarkable exothermal reaction of about 16 mW/mg above 1180°C. The mixed powder SiC+GeO₂ turned to black in color and crystalline fragments after the measurements. Though the weight gain is faster than pure SiC but is decreased above 1180 °C as is shown in the inset of Fig. 4(b). It is suggested that the SiC starts to be oxidized to gain weight above 1000 °C and then reacted with GeO₂ to form a new phase. This was validated by data from XRD.
Figure 2: Comparison of TGA/DSC profiles of submicron and nano SiC powders (a) and SiC+Y2O3 mixtures with submicronic or nano sized SiC (b). Note here that the weight gain values are given with respect to the SiC weight, while the DSC values are as obtained.

Figure 3: TGA/DSC data of submicron SiC and additives, Al2O3, TiO2, GDC and Ta2O5, which show little influence on SiC oxidation. Note here that the weight gain values are given with respect to the SiC weight, while the DSC values are as obtained.
In the case of SiC+Y₂O₃ and SiC+ZnO in Fig. 5, small exothermic peaks are observed around 1050 °C and around 950 °C, respectively, at which or slightly lower temperature weight gain started. As already described above, the weight loss in SiC+Y₂O₃ can be attributed to the evaporation of absorbed water molecules from the Y₂O₃ surface, which is due to the small particle size of this powder. It is noteworthy that the weight gain of these mixtures is larger than that of pure SiC. As the only weight gain comes from oxidation of SiC, the result suggests that oxidation kinetics can be enhanced by these additives.

![Graph](image.png)

Figure 4: TGA/DSC data of submicron SiC and additives, which show remarkable differences in weight and/or DSC from those of pure SiC. (a) CaO, BaO, La₂O₃, (b) GeO₂.

Fig. 6 (a) shows XRD patterns of SiC powder before and after TGA measurements. Although the intensities of the XRD patterns before and after TGA/DSC are not numerically comparable in the measurement condition, they can be used for qualitative comparison. Remarkable decrease in intensity is noted but no additional peak appeared after TGA in Fig. 6. The powder color change from dark gray to light gray and the weight gain at 1050 °C in TGA demonstrate SiC oxidation, i.e. formation of new oxide phase, such as SiO₂. However no SiO₂ phase, either glassy phase or crystalline phase, was observed in XRD. Since diffraction of glassy phase is very broad and very weak in general, it is suggested most of the oxidized phase was in glassy phase. XRD results of SiC and additive mixtures which showed similar behavior in TGA/DSC, SiC+Al₂O₃, SiC+GDC and SiC+Ta₂O₅, confirmed that no new phase was formed in
the mixtures. In the case of SiC+TiO$_2$, however, it was found that the starting powder of TiO$_2$ was mainly anatase, which turned to rutile phase after TGA/DSC. It is known that anatase may turn to rutile phase at about 800 °C$^{20}$ and the rutile is the most stable TiO$_2$ phase.

![TGA/DSC data of SiC and additives: Y$_2$O$_3$ and ZnO](image)

Figure 5: TGA/DSC data of SiC and additives: Y$_2$O$_3$ and ZnO

![XRD patterns (zeroed base line) of SiC powder (a) and SiC+Al$_2$O$_3$ mixture (b) before and after TGA/DSC measurements.](image)

Figure 6: XRD patterns (zeroed base line) of SiC powder (a) and SiC+Al$_2$O$_3$ mixture (b) before and after TGA/DSC measurements.

The powder mixtures of SiC+CaO, SiC+BaO and SiC+La$_2$O$_3$ show weight losses between 100 and 700 °C, which may be attributed to water or carbon dioxide desorption adsorbed on the secondary additive materials. As shown in Fig. 7 (a), it is confirmed that CaO in the mixture had Ca(OH)$_2$ and CaCO$_3$ phases which may have been formed in ambient atmosphere before the measurement. The SiC+CaO mixture shows a significant change in XRD pattern. The hydroxyl and carbonated compounds disappeared and calcium silicate phase, Ca$_3$(SiO$_3$)$_2$ and CaSiO$_3$, were found after the TGA measurement. Note here that only Ca$_3$(SiO$_3$)$_2$ is indicated in the figure as a main silicate phase, while CaSiO$_3$ phase is much smaller in intensity. SiC+BaO and SiC+La$_2$O$_3$
showed similar behavior and many silicate phases, namely BaSiO₃, Ba₂SiO₄ and Ba₂Si₃O₈, were found for SiC+BaO mixture, while La₂O₃ and small amount of L₂₉₃₃(SiO₄)₂O₂ were detected for SiC+La₂O₃ mixture after TGA/DSC measurements.

The results for SiC+GeO₂ indicate that GeSi phase was formed (Fig. 7 (b)), which is consistent with the TGA/DSC result. Since the measurement temperature was higher than the stable melting point (1116 °C) and the metastable melting point (1086 °C) of GeO₂, GeO₂ may have reacted with SiC to form the GeSi phase rather to promote the SiC oxidation above this temperature. Though the brazing and SOFC operating temperatures are lower than those melting points, it would be risky to use GeO₂ as a promoting additive.

The XRD data in Fig. 8 for SiC+Y₂O₃ and SiC+ZnO demonstrate that metal silicate phases, Y₂SiO₅ and Zn₂SiO₄, are formed in the mixtures. For both mixtures, remarkable decrease of SiC diffraction intensity is also noticed. Considering high molar ratio of these metal silicates (metal:Si=2:1) than the composition of the mixed powder (metal:Si=1:1), it is possible that SiC oxidized in SiO₂ phase at the same time. This could probably be formed in a glassy phase, since no crystalline SiO₂ is observed by XRD.

The interaction between SiC and the additive was further investigated by the microscopic Raman spectroscopy. In Figs. 9, Raman spectra of nano-SiC and nano-SiC+ZnO mixture are given. Si-C vibration modes are observed between 700 and 1000 cm⁻¹. These are corresponding to the TO and LO phonons of Si-C, whose intensity is significantly weaker and broader than that of bulk crystalline SiC because of the small grain size²²,²³. The broad structure above 1000 cm⁻¹ is corresponding to the stretching modes of the C-C bonds²⁴. Such C-C vibrations are of amorphous or graphite carbons on the surface²⁵, which can be present on nano-sized SiC powder. Raman spectrum of nano-SiC and ZnO mixture is very similar to that of pure nano-SiC. This is due to significantly low raman scattering intensity of ZnO.
Figure 8: XRD patterns of the mixtures before and after TGA/DSC (zeroed base line):
(a) SiC+Y_{2}O_{3}, (b) SiC+ZnO.

Figure 9: Raman spectra of nano SiC (a) and nano SiC+ZnO (b) heat treated at 1050°C in air for different times and after TGA measurement. The peaks appeared at 868, 903 and 942 cm\(^{-1}\) are the Raman modes of Zn_{2}SiO_{4}.

After annealing in ambient air for 5 hours, intensity of the C-C vibration modes of nano SiC powder was increased, while little change of the Si-C modes was noticed. On the other hand, the SiC-ZnO mixture showed two major changes after TGA measurement. One is intensity decrease of Si-C modes and the other is intensity increase of C-C modes. The latter is similar to that of nano-SiC powder, however, the former is possibly to the influence of ZnO, as is observed.
in TGA and XRD results in which promotion of SiC oxidation is suggested. When SiC-ZnO mixture was annealed in ambient air, Si-C modes is further decreased by annealing time and new Raman peaks were observed. The new peaks, indicated by vertical lines in Fig. 9(a), are of Zn$_2$SiO$_4$ phase $^{25}$, which is consistent with the XRD results. Although the peak intensity is low, the silicate phase is also detected after TGA as indicated in Fig. 9(a). The stretching modes of the Si-C and C-C bonds are significantly weaker when the mixture is annealed for 5 hours in contrast to the case of nano-SiC. This suggests that higher kinetics of the healing reaction can be attained in the case of the mixture.

From these data Y$_2$O$_3$ and ZnO appears as potential secondary additives: BaO should be excluded because of its high reactivity and lack of stability. CaO and La$_2$O$_3$ are also not suitable secondary additives for the self-healing coating, since they are also instable and they do not show any remarkable promotion for the SiC oxidation. The melting point of GeO$_2$ is very close to the brazing temperature. Therefore, it is risky to be reduced to form SiGe phase like in the TGA measurement. No other secondary additive promoted the oxidation reaction or reactive phase formation. The addition of Y$_2$O$_3$, despite of its weight loss due to the evaporation of absorbed water molecules in the Y$_2$O$_3$ surface, can promote the weight gain – thought the reaction temperature was almost identical to SiC alone. It is evident that ZnO is the most promising candidate which initiated and promoted the SiC oxidation at temperatures below 1000°C. Therefore, ZnO and Y$_2$O$_3$ would be considered further as the most promising secondary additives for the coating. Although Al$_2$O$_3$ alone did not exhibit reaction with SiC or promotion of the SiC oxidation, it is considered as a good catalyst for vitreous phase formation and therefore Al$_2$O$_3$ has been also selected as a candidate additive for the further investigation.

Self-Healing Coatings

Figure 10 illustrates the structure of self-healing air plasma sprayed coating made of MgAl$_2$O$_4$ as gray matrix, and SiC+Y$_2$O$_3$ as bright splats of additive material. In the higher magnification micrograph of a additive splat (Fig. 10 (b)), it can be observed that the dark particles of SiC are embedded in the brighter Y$_2$O$_3$. The self-healing coatings were fractured and heat treated at 1050°C in air for 1, 5 and 10 hours. As it can be seen from the micrographs of the as-sprayed fractured coating and the ones heat treated for one hour in Figs. 11 (a) and (b), crack healing was already observed after 1 hour. However limited numbers of cracks with median length of less than 1 μm were healed. This can also be attributed to a “thermal healing”. Hence, despite indication from the SiC+Y$_2$O$_3$ data that a reactive phase formation may already occur after one hour, it was not conclusive when tested in a plasma sprayed coating for 1 hours. On the other hand, reactive vitreous phase formation was evident after 5 and 10 hours of heat treatment and larger defects could be healed (Fig. 12 (a to d)). Within a matrix of parent ceramic, it can be expected that the additive material would have access to lower concentration of oxygen and slower transformation kinetics.

The resistance data of pure spinel and spinel + 20wt% (SiC+Y$_2$O$_3$) coatings as a function of temperature is given in Fig. 14, revealing that the self-healing additive did not deteriorate the insulating properties of the coatings. The coefficient of thermal expansion (CTE) data, as summarized in Table 2, established that CTE of the spinel coating decreased as a function of SiC content which can be explained by the lower CTE of SiC. In the presence of composite additive (SiC+Y$_2$O$_3$), the CTE values were in between that of pure spinel and spinel+20wt%SiC which can be owing to the comparable CTE of Y$_2$O$_3$ to that of spinel. The coating, heat treated at 1050°C in air for 10 hours, had a comparable CTE to as-sprayed counterpart.
Figure 10: SEM of (a) self-healing coating: Bright additive particles are distributed in dark spinel matrix. (b) a splat of additive material. Dark particles are SiC and bright zone is Y$_2$O$_3$.

Figure 11: (a) SEM micrographs of self-healing ceramic coating of in as-sprayed condition, and (b) of same zone and magnification after heat treatment at 1050°C for 1 hour in air.
Figure 12: (a and c) Micrographs of fractured self-healing ceramic coating in as-sprayed condition, and (b and d) same zone and magnification after heat treatment at 1050°C for 5 hours (b) and 10 hour (d) in air.

Figure 13: Electrical resistance values for MgAl2O4 and MgAl2O4+20wt% (SiC+Y2O3) coatings.
Table 2: CTE values of spinel and spinel+additive coatings

<table>
<thead>
<tr>
<th>Coating Material</th>
<th>Technical $\alpha$ ($10^{-6} / \text{K}^{-1}$)</th>
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<tbody>
<tr>
<td></td>
<td>At 800°C</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>8.31</td>
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<tr>
<td>MgAl$_2$O$_4$+ 5wt%SiC</td>
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<td>MgAl$_2$O$_4$+ 20wt%SiC</td>
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<td>MgAl$_2$O$_4$+ 20wt% (SiC+Y$_2$O$_3$) - As-sprayed</td>
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<tr>
<td>MgAl$_2$O$_4$+ 20wt% (SiC+Y$_2$O$_3$) - After heat treatment</td>
<td>8.06</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The current work attempted to incorporate self-healing capability in MgAl$_2$O$_4$ ceramic coatings by introducing healing additives. Moreover, as the coating was employed in solid oxide fuel cells, it was targeted to select suitable additives that can engender healing at cell operating temperature, typically 800°C. As healing additive, micro-sized or nano-sized SiC was investigated with addition of one of the following BaO, CaO, ZnO, Y$_2$O$_3$, Al$_2$O$_3$, La$_2$O$_3$, TiO$_2$, GeO$_2$, Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (GDC) or Ta$_2$O$_5$. It was established that decreasing the size of SiC particles has only marginal effect on promoting its oxidation or reaction with secondary additives. Moreover, independent of the size of the particles, with only SiC as additive, any healing reaction may be observable after heat treatment at 1050°C for more than 10 hours; SiC was still not fully converted in SiO$_2$ in exposed areas. Addition of Y$_2$O$_3$ was established to promoted reaction kinetics. Though the temperature of reaction temperature remained comparable to SiC, i.e. above 1000°C, the reaction time was reduced to 1 hour. However, once embedded in a matrix of coating, healing was demonstrated at 1050°C but for dwell time of 5 hours and more, 10 hours treatment was opted for healing. Functional properties of the self-healing insulating coating, CTE and resistivity, remained comparable to spinel coatings. For sub-1000°C healing, promising healing results were attained when ZnO instead of Y$_2$O$_3$ was used as secondary additive. TGA/DSC data revealed that temperature of healing reaction could be reduced to 950°C. This, however, need to be established with further trials which are on-going. The coatings of MgAl$_2$O$_4$ with SiC+ZnO will also be investigated.
REFERENCES


