On the use of TiC as high-temperature healing particles in alumina based composites

Shunsuke Yoshioka¹, Linda Boatemaa², Sybrand van der Zwaag³, Wataru Nakao⁴, Willem G. Sloof².

¹ Graduate School of Engineering, Yokohama National University, 79-5, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

² Department of Material Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD Delft, The Netherlands

³ Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands

⁴ Faculty of Engineering, Yokohama National University, 79-5, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Abstract

We report on the use of TiC particles as high temperature healing agent in alumina based composites. The selection of TiC was based on a theoretical analysis of its high temperature stability in contact with Al_2O_3 , its volumetric expansion upon oxidation and the adhesion between the reaction product TiO_2 with Al_2O_3 . Fully dense 15 and 30 volume percent TiC-Alumina composites were made by Spark Plasma Sintering. Initial damage was produced by Vickers indentations. The strength recovery was determined for temperatures between 400 and 800 °C. The mechanical measurements were complemented by microstructural characterization of the base material and the healed cracks.

1. Introduction

In recent years there has been a lot of research into the autonomous healing of surface cracks in ceramics [1-23] and metallo-ceramics (MAX phase materials) [24-32] by oxidative filling of cracks when exposed to high temperatures. In the case of metallo-ceramics the healing is of the so-called *intrinsic* self healing type [33, 34], meaning that the metallo-ceramic itself is capable of undergoing

an oxidative reaction resulting in filling of the crack and partial or complete recovery of the tensile strength. In the case of oxidic ceramics, such a reaction is impossible as the matrix is already in its oxidized state and cannot undergo any further reaction. Hence, for such materials the ability to heal surface cracks relies on the presence of intentionally embedded discrete particles called 'healing agents' which show a desirable response to high temperature exposure to oxygen containing gasses. Earlier works on such *extrinsic* healing ceramic systems focused on the oxidation of granular SiC particles embedded in several oxidic ceramic matrices. Harmer *et al.* observed that indentation induced cracks in alumina/ 5-vol.% SiC could be healed partially by means of annealing at 1300 °C for 2 h [1-2]. However, they also noted that the formed SiO₂ could not seal the pre-cracks fully due to the low SiC particle content. Ando *et al.* were the first to report in detail on the self-healing behaviour of SiC particles containing alumina matrix composites as a function of temperature and annealing time [3-5]. It was shown that alumina/ 15 vol.%-SiC composites can attain a complete strength recovery by annealing in air at 1300 °C for 1 h or at 1200 °C for 10 h [3]. Ando *et al.* demonstrated that other structural ceramic matrix composites containing SiC particles as self-healing agent, such as mullite/ SiC [6-7], Si₃N₄/ SiC [8-9], ZrO₂/ SiC [10-11], also show self-healing behaviour. They demonstrated that mullite-based composites containing 20 vol.% of SiC particles could achieve complete strength recovery by various heat treatments at rather high temperatures, such as annealing for 5 h at 1200 °C or for 1 h at 1300 °C [7]. On the other hand, Si₃N₄/ 20 vol.%-SiC and ZrO₂/ 20vol.%-SiC composites recovered their room-temperature strength by annealing at relatively low temperatures e.g. at 1000 °C for 1 h in Si₃N₄/ SiC [9] and at 800 °C for

30 h in ZrO₂/ SiC composite [10], respectively. However, it was also observed that Si₃N₄/ SiC specimens annealed above 1400 °C and ZrO₂/ SiC specimens annealed above 1000 °C lose their mechanical properties due to excessive corrosion. In general, relatively high annealing temperatures (mostly above 1200 °C) are required for adequate oxidation of SiC particles in order to seal the crack-gap and to recover mechanical integrity of ceramics matrix composites.

Several methodologies have been proposed with the aim of enhancing the crack-healing ability of SiC containing composites. The first attempt involved the inclusion of SiC whiskers in order to simultaneously improve the fracture toughness, K_{IC} , and self-healing ability of the composite [12-15]. Nakao et al. [12] observed that the K_{IC} value of 20 vol.% SiC-whisker containing alumina based composites ($K_{IC}=5.6 - 5.7 \pm 0.2 \text{ MPa} \cdot \text{m}^{1/2}$) is considerably higher than that of monolithic alumina ($K_{IC}=3 - 4 \text{ MPa} \cdot \text{m}^{1/2}$). Furthermore, it was found for alumina with 20 vol.%-SiC whisker that the minimum healing temperature at which the strength of the composite can recover within 1 h is 100 °C lower than that of alumina/ granular SiC composites. The effect was attributed to the larger surface area of the SiC whiskers per unit of volume. An alternative method to enhance the healing ability is downsizing of the healing agent [16-17]. Nakao *et al.* reported that alumina composite containing 18 vol.% of nano-SiC having a diameter of 10 -30 nm can attain full strength recovery within 10 h annealing at 950 °C [17]. So, depending on the morphology and size of the SiC fraction the minimum required temperature for the complete strength recovery can be varied in range of 950 – 1300 °C.

More recently, some advanced healing agents replacing SiC have been proposed. Abe *et al.*

developed alumina/ 10 vol.-%-NiAl composites which can heal cracks within 10 h in 1250 °C [18]. Nanko *et al.* proposed the use of nano-Ni powder as healing agents [19-21] and Maruoka *et al.* observed that alumina/ 5 vol.-%-nano Ni composites can attain full strength recovery by annealing for 1 h at 1200 °C [21]. In order to achieve full healing at lower temperatures, Ti containing self-healing agents have been proposed. For example, mullite with 15 vol.-%-TiSi₂ composites can achieve full strength recovery by annealing at 600 °C for 10 h [22]. The potential of Ti containing MAX phase, Ti₂Al_{0.5}Sn_{0.5}C, as healing agent has been studied by Bei *et al.* and they found that alumina with 20 vol.-%-Ti₂Al_{0.5}Sn_{0.5}C composites can recover their strength fully by annealing for 5 h at 900 °C [23].

A potentially interesting self-healing system not yet studied in any detail is presented by alumina composites containing TiC particles as the healing agent. The results of a theoretical analysis of the prevailing reactions and some experimental crack healing studies are described below. The results clearly demonstrate that TiC is a potentially attractive healing agent for alumina matrices.

2. Theoretical analysis of the healing potential of TiC in an alumina matrix

In a recent publication Farle *et al.* [30] presented a theoretical frame work to predict the (intrinsic) healing ability of 59 metallo-ceramics on the basis of a number of fundamental physical parameters such as the thermal stability in an oxidative environment, the diffusion kinetics, the

volume expansion upon oxidation, the work of adhesion between the reaction product and the matrix material and the CTE and modulus of the reaction product in relation to that of the parent phase. The first four parameters give information on the potential crack filling behaviour while the two latter parameters give information on the quality of the mechanical properties of healed cracks upon re-loading. In the present analysis we follow their analysis but focus on the properties relevant for extrinsic self-healing systems based on embedded granular healing particles.

2.1 Thermodynamic stability of TiC

The thermodynamic stability of TiC in the presence of oxygen and that of its intended reaction product TiO_2 in the presence of Al_2O_3 is calculated using FACTSAGE (CRCT-ThermFACT Inc. & GTT-Technologies). In Figure 1 the thermodynamic stability of TiC in air as a function of temperature is shown. The figure shows that thermodynamically speaking TiC can transform into TiO_2 even at room temperature.

Figure 1 Thermodynamic stability of TiC in air versus that of TiO₂ as a function of temperature.

The calculated phase diagram for the TiO₂ and Al₂O₃ system is shown in Figure 2 for the temperature window 1000-2000 °C. This figure shows that there are no deep eutectica and that the lowest temperature at which a liquid phase is present is about 1700 °C. Hence, this temperature sets the upper healing temperature ever to be considered for this system.

Figure 2 TiO₂-Al₂O₃ pseudo phase diagram (i.e. excluding oxides TiO₂-x, Ti₃O₅, Ti₂O₃, TiO).

According to the phase diagram, at temperatures between 1270 °C and 1800 °C TiO₂ can react with

Al₂O₃ and form the intermediate compound Al₂TiO₅. This reaction product resembles the mullite formed in the SiO₂ – Al₂O₃ system. There are no reports on the reaction between SiO₂ and the alumina matrix formation so that the formation of mullite at the crack-healed can be assumed to be quite slow or even absent. We postulate that this also applies to the Al₂TiO₅ compound. So provided the healing time is not too long, the temperature window 1270-1600 °C could be available for self-healing reactions. Based on the pseudo phase diagram, there are no further reactions between TiO₂ and Al₂O₃ below 1270 °C and this indicates that provided all other conditions are met, the temperature domain below 1270 °C is suitable for self-healing reactions and prolonged material use.

2.2. Relative volume expansion (RVE)

Successful crack filing due to solid state chemical reactions requires that the molar volume of the reaction product is larger than that of the starting healing material in order to i) (fully or partially) fill the crack, ii) locally reconnect opposing crack faces and iii) re-establish mechanical integrity. The volumetric growth is expressed as the relative volume expansion (RVE). In this work we look at the decomposition of a carbide into a metallic oxide as presented by the following reaction:

Hence,

$$RVE [\%] = \frac{V_{MO_2} - V_{MC}}{V_{MC}} \times 100 \quad \dots(2)$$

Here, V_x means molar volume of substance X. The value of V_x can be calculated based on the following equation:

$$V_x [\text{cm}^3/\text{mol}] = \frac{C [\text{\AA}] \times 10^{-24}}{N [-]} \times N_A [\text{mol}^{-1}] \quad \dots(3)$$

Here, C means the cell volume of substance X and N means the number of unit in each cell. The crystal data used are listed in Table 1.

Table 1 Reference data used for RVE calculation.

Compound	Cell Volume $C [\text{\AA}^3]$	Unit number $N [-]$	Molar volume $V_x [\text{cm}^3/\text{mol}]$	Reference (PDF No.)
SiC	82.77	4	12.5	01-075-0254
TiC	81.07	4	12.2	04-004-2919
SiO ₂ (Cristobalite)	176.54	4	26.6	01-082-0512
TiO ₂ (Rutile)	62.43	2	18.8	00-021-1276

The calculated RVE of TiC is shown in Table 2. As seen in Table 2, the RVE of TiC is more than 0 %, which means that TiC can indeed create the extra volume required for filling the crack-gap upon oxidation.

Table 2 Calculated RVE value of TiC and SiC.

Reaction	Relative Volume Expansion (RVE) [%]
SiC + 2O ₂ → SiO ₂ (Cristobalite) + CO ₂	113.3
TiC + 2O ₂ → TiO ₂ (Rutile) + CO ₂	54.0

According to previous studies [3-4], 15 vol.% fraction of SiC was sufficient for filling the surface crack with 100 μm and attain full strength recovery of alumina/ SiC composite. Assuming the local crack

facing distance of the induced indentation cracks to be the same one can argue that the optimal volume fraction of TiC self-healing agent should be of the order of 30 vol.% in order to realize a comparable self-healing of TiC/ alumina composite and to compensate for the lower RVE value. Hence, our experimental studies focus on 15-30 vol.%-TiC containing Al_2O_3 composites.

2.3. Work of adhesion

In order to achieve complete strength recovery, the energy required to separate the crack-filling oxide from the alumina matrix should be comparable or greater than the cohesion strength of the alumina matrix. This adhesion energy of the interface between matrix/ crack-filling oxide interface is defined as the 'work of adhesion'. This work of adhesion can be expressed by [35]:

$$W_{\text{ad}} = -(\gamma_{\text{matrix}}^{\text{surf}} + \gamma_{\text{oxide}}^{\text{surf}}) + \gamma_{\text{matrix/oxide}}^{\text{interface}} \quad \dots(4)$$

where, $\gamma_{\text{matrix}}^{\text{surf}}$ and $\gamma_{\text{oxide}}^{\text{surf}}$ mean the surface energy of matrix and oxide, and $\gamma_{\text{matrix/oxide}}^{\text{interface}}$ means the interface energy between matrix/ crack-filling oxide interface. The value for the interface energy has been estimated from the interaction energies of the atoms located at each site of the interface [36, 37]. The interaction energies were calculated from solution enthalpies of an element at one site of interface dissolved in another element at the other site of the interface. Details of the calculations can be found elsewhere [38].

The calculated work of adhesion for relevant interfaces are shown in Figure 3.

Figure 3 Calculated works of adhesion for relevant interfaces.

As justified in Section 2.1, in the present analysis the formation of Al₂TiO₅ is ignored. The work of adhesion for the Al₂O₃/ TiO₂ interface (4900 mJ/m²) and that for the TiO₂/ TiO₂ interface (5630 mJ/m²) are greater than that for the Al₂O₃/ Al₂O₃ interface (4090 mJ/m²). The latter two values represent the cohesion of the crack filling and matrix phase, respectively. It means that the crack-healed part in alumina/ TiC could be stronger than the alumina matrix itself. To put these values in perspective we also report the work of adhesion between Al₂O₃/ SiO₂ interface (4020 mJ/m²) which is a well-known self-healing ceramic system.

From these calculations, it can be postulated that the alumina/ TiC composites will attain full strength recovery once the crack is filled up adequately with the TiO₂ formed.

2.4. Comparison of the thermal expansion coefficients

Even if the crack is fully filled by the formation of an oxidic phase at the healing temperature, this is no guarantee that a strong and reliable bond is formed when the sample is exposed to a wide range of temperatures. Differences in coefficient of thermal expansion (CTE) between the matrix and the material formed in the crack as a result of the healing reaction may lead to local stresses. Hence, it is important to compare the CTE's of matrix (Al_2O_3), healing agent (TiC) and crack-filling oxides (TiO_2). Relevant average CTE values are listed in Table 3, together with the related values for alumina /SiC composites. The dependence of CTE on crystal orientation was not taken into account as the material deposited in the crack is polycrystalline.

Table 3 Thermal expansion coefficients of relevant compounds in alumina /TiC and alumina/ SiC composite.

Compound	Temperature Range [°C]	CTE $\times 10^{-6}$ [°C ⁻¹]	Reference
Al_2O_3	1000 - 1600	7.5 ± 0.4	[39]
	20 - 2025	7.3 - 8.3	[40]
TiC	23 - 848	$6.99 \pm 0.34 - 7.61 \pm 0.20$	[41]
	1000 - 2600	8.31 ± 0.68	[39]
SiC	25 - 1000	3.2 - 5.1	[42]
	1000 - 1600	5.68 ± 0.11	[39]
TiO_2 (rutile)	30 - 650	7.249 - 8.816	[43]
	20 - 1610	8.9 - 11.1	[40]
SiO_2 (Cristobalite)	100 - 500	10.9	[44]
	500 - 1000	1.7	[44]

According to Table 3, the CTE values of the matrix, the unreacted healing agent and the

relevant crack-filling oxides in the alumina /TiC system considered are in the range of 6.65×10^{-6} to $11.1 \times 10^{-6} [^{\circ}\text{C}^{-1}]$. The maximum mismatch value is $4.45 \times 10^{-6} [^{\circ}\text{C}^{-1}]$ between TiC and TiO_2 at temperature region from room temperature to 500 °C. In contrast, the maximum mismatch value in the reference alumina /SiC system is $7.7 \times 10^{-6} [^{\circ}\text{C}^{-1}]$ between SiC and SiO_2 at temperature region from room temperature to 500 °C, and $6.6 \times 10^{-6} [^{\circ}\text{C}^{-1}]$ between alumina matrix and SiO_2 at above 500 °C. Considering there are no reports on the spontaneous fracture of alumina /SiC self-healing ceramics due to thermal expansion mismatch, it can be proposed that the effects of the CTE mismatch in the alumina /TiC composites on structural integrity can be ignored at this stage.

2.5. Comparison of the elastic properties

A healed crack in a ceramic compound may not only be exposed to the thermal stresses induced by temperature excursions but may also be exposed to mechanical stresses due to external loading. In this case it is important to compare the elastic moduli of the matrix, the healing agent and the decomposition product. The Young's moduli of relevant (polycrystalline) compounds in alumina /TiC and alumina/ SiC composites are listed in Table 4.

Table 4 Young' modulus of related compounds in alumina /TiC and alumina/ SiC composite.

Compound	Specimen	Density [-]	Young's modulus [GPa]	Reference
Al_2O_3	Sintered bulk	≥ 99.6	380-410	[45]
	Sintered bulk	≥ 99.8	380-405	[45]
	Sintered bulk	≥ 99.5	398-400	[45]
	Sintered bulk	≥ 99.6	340-380	[45]
	Sintered bulk	≥ 99.0	340-380	[45]
TiC_x ($x < 1$)	Thin firm	-	< 460	[46]
SiC	Sintered bulk	≥ 0.98	415	[47]
TiO_2	Cristalized thin firm	-	85	[48]
SiO_2 (Cristobalite)	Natural single crystal	-	65.2	[49]

Considering that Young's modulus of TiC_x is depends on the carbon level [46], it can be stated that the Young's modulus of TiC_x is more or less comparable to alumina matrix, as is the case for SiC. In contrast, the modulus of SiO_2 and TiO_2 is considerable lower than that of matrix. Based on the values reported and given that full strength recovery has been attained in alumina/ SiC system, it is expected that the alumina/ TiC can also yield comparable self-healing levels. Early cracking along the healed interface is not very likely to occur unless at higher macroscopic stress levels.

In conclusion, based on the theoretical analysis presented above it is to be expected that autonomous high-temperature oxidative healing of the mechanical integrity of an Al_2O_3 composites filled with (10-30 vol %) TiC particles should theoretically be possible.

3. Experimental

Alumina matrix composites containing 15 vol.% TiC and 30 vol.% TiC, named Al15TiC and

Al₃₀TiC respectively, were prepared and their strength recovery at room temperature as a function of the healing temperature was studied under the conditions specified below. Furthermore, the microstructural changes responsible for the strength recovery were also determined.

3.1. Sample preparation

Alumina raw powder (AKP-50, Sumitomo Chemical Co., Ltd.), and TiC powder (STD120, H.C. Starck GmbH) were used as starting materials. The initial average sizes were 0.2 and 2 μm , respectively. Ball-milling of TiC powder was conducted for 36 h in isopropanol with $\varnothing 10$ mm WC ball and a WC jar, resulting in an average particle size of 0.3 μm . Alumina powder and ball-milled TiC powder were mixed at either 15 vol.% or 30 vol.% in isopropanol using $\varnothing 5$ mm alumina balls and a 1000 ml plastic bottle. After 12 h mixing, the mixed powder was dried in the oven for 24 h at 80 °C. The dried powder was sieved with a $\varnothing 200$ μm mesh powder sieve. The sieved powder was densified by means of spark plasma sintering (HP D 25-SD furnace, FCT Systeme GmbH) with a $\varnothing 40$ mm carbon mould at 1500 °C for 15 min. in vacuum condition under 35 MPa. The heating rate was 10 °C/min while natural cooling was used to cool down from the maximum temperature. The typical thickness of the samples was about 5 mm. The relative density of the sintered bulk materials as measured by Archimedes' method was more than 99 %. The sintered discs were cut into rectangular samples with a dimension of 3 x 4 x 23 mm for four-point bending tests. Samples were polished in various steps with a final polish using a diamond paste with a particle size of 0.25 μm .

3.2. Strength recovery tests

In order to study the strength recovery of Al₁₅TiC and Al₃₀TiC as a function of the annealing temperature, the strength values of three types of specimen (smooth specimen, pre-cracked specimen and healed specimen), were determined. Smooth specimen refers to samples without any induced damage prior to testing. Pre-cracked specimen are specimen with a standardized pre-crack at the centre of the surface introduced by Vickers' indenter. The indentation force was 20 N and the introduced crack had a surface length of about 100 μm for both sets of samples. The surface crack opening distance of these cracks could not be established with any real accuracy but was estimated to vary between 0.1 to 0.5 μm . The two sets of radial indentation cracks are either perpendicular or parallel to the longest dimension of the bend test samples. No strong interaction between the indentation induced radial cracks and the healing particles was observed. The healed specimens are pre-cracked and have been annealed for 1 h in air at temperatures ranging from 400 to 1000 °C.

The strength of each sample was measured by means of an auto aligning four-point bending test using the set-up shown in Figure 4.

Figure 4: Self-aligning four-point bending set-up used.

The upper and lower span between the supporting 2 mm diameter steel rollers was 20 and 10 mm, respectively. The specimen was mounted such that the maximum tensile stress was applied to the pre-crack or healed crack part. All tests were conducted at room temperature and with a cross-head displacement velocity of 0.5 mm/min.

3.3 Structure characterisation

The external appearance of the healed cracks was recorded with a laser microscope (KEYENCE, VK-X) and analysed using image software. The chemical composition of the reaction product formed in the crack was determined using Electron Probe Micro Analysis (EPMA) using a JXA-8530F JEOL Ltd microprobe. To enable such measurements, the surface oxidation layer was removed by using a focused ion beam (JIB-4501, JEOL Ltd.). The crystal structure of the various phases in the samples prior and after thermal annealing was determined using XRD (ULTIMA IV, Rigaku Co.) operated with

CuK α radiation.

4. Results and Discussion

4.1 Strength recovery

The results of strength recovery tests for both Al15TiC and Al30TiC are shown in Figure 5.

Figure 5 Flexural strength values of Al15TiC and Al30TiC samples after healing for 1 h in air at the reported temperature.

The averaged strength of smooth specimens at room temperature was 526 MPa for Al15TiC and 598 MPa for Al30TiC. The averaged strength of pre-cracked specimens was 208 MPa for Al15TiC and 199 MPa for Al30TiC, i.e. more or less equal and in accordance with the equal dimensions of the indentation induced cracks. Figure 5 shows that annealing at 400 °C already leads to some recovery

of the strength (this could be due to oxidative healing but thermal blunting of the crack tip may also play a role). This lowest temperature at which partial strength recovery is observed is considerable lower than that observed for alumina/ SiC composites. Annealing at 800 °C led to a complete recovery of the strength for both sets of samples.

4.2 Microstructural observations

Laser microscope images of pre-cracked area before and after annealed at each condition are shown in Fig. 6-8 for annealing temperatures of 400, 600 and 800 °C respectively.

Fig. 6 Laser microscope image of pre-cracked area of Al₃₀TiC (a) before annealing (b) after annealing at 400 °C for 1h. Arrows indicate the end-points of the radial cracks.

Fig. 7 Laser microscope image of pre-cracked area of Al30TiC (a) before annealing (b) after annealing at 600 °C for 1h. Arrows indicate the end-points of the radial cracks.

Fig. 8 Laser microscope image of pre-cracked area of Al30TiC (a) before annealing (b) after annealing at 800 °C for 1h. Arrows indicate the end-points of the radial cracks.

Figure 6 (sample annealed at 400 °C) shows no sign of surface oxidation and the cracks remain nicely visible. In contrast, Figures 7-8 (annealing temperatures 600 and 800 °C, respectively) show clear signs of surface oxidation at the location of the TiC particles intercepting the external

surface and the crack is no longer discernible.

Figure 9 shows the SEM image and backscattered electron image around the healed-crack area of the healed specimen at 800 °C for 1 h after removing the surface oxidation layer by mechanical polishing using 0.25 µm diamond past. The healed crack is indicated by arrows in both figures. Taking the result of Energy Dispersive X-ray Spectrometry into account, it is clear that the crack is fully filled with the titanium oxide formed. It is interesting to note that the titanium oxide can be found also at locations in the crack well away from intersected TiC particles. This lateral spreading of the oxide along the crack is very advantageous for the healing efficiency. It also should be noticed that TiC healing-agent particles nearby the crack surface are still intact. In conclusion: Figure 9 confirms that the crack is fully filled up with titanium oxide upon 800 °C annealing for 1 hour.

Fig. 9 Backscattered electron image of healed- crack area of Al₃₀TiC annealed at 800 °C for 1h. The external oxidation layer was removed by minimal mechanical polishing.

The results of XRD analysis of the as-synthesized and the annealed samples are shown in Figure 10. Some contamination of TiC with WC was expected due to the ball milling treatment, but no traces of WC were detected. The diffractogram after 1 h annealing at 400 °C did not differ from that of the as-synthesized specimen. For higher annealing temperatures clear signs of Rutile were observed, but Anatase and Brookite were not detected. TiC was still detectable in the sample annealed at 800 °C. This indicates that the surface is not fully covered with TiO₂ yet and also TiC is still intact nearby the surface. Also, the formation of Al₂TiO₅ was not detected even annealing at 800 °C. Those results correspond to the discussion on the surface observations shown above and the possibility of Al₂TiO₅ formation during annealing at high temperatures in section 2.1.

Fig. 10 XRD patterns of Al₃₀TiC in the pristine state (smooth) and after annealing for 1 h at the temperatures indicated.

Finally, it should be mentioned that at 800 °C full strength recovery was observed for both Al₁₅TiC and Al₃₀TiC material while it was postulated on the basis of the RVE calculations that in the case of 15 vol.% TiC (i.e. Al₁₅TiC material) the additional volume created by the oxidation of 15 vol.% TiC might be insufficient to fully fill and heal the cracks. Clearly the critical volume concentration for full crack filling depends not only on the length of the crack but also on the average local crack facing distance (i.e. the total initial open crack volume). [50]. The full healing of the Al₁₅TiC material may well be attributable to either more narrow indentation cracks than assumed or easier long-range transport

of the Ti atoms along the crack and through the matrix. Complicated 4D nano-CT tomography measurements of the type reported elsewhere for high temperature crack healing in MAX phase material [51] would be required to establish the degree of crack filling in this material also below the surface.

5. Conclusion

This paper aimed to study the capability of TiO_2 as a crack-filling oxide for self-healing oxidic ceramics and the self-healing property of alumina/ TiC composites in particular. A detailed theoretical analysis of the healing reaction and the intrinsic properties of the reaction products revealed that TiC is indeed a potentially attractive healing agent for extrinsic self-healing ceramic systems. Experimental studies on SPS sintered Al_2O_3 -TiC composites containing 15 and 30 vol% TiC particles with a typical diameter of 0.3- 5 μm showed complete tensile strength recovery by annealing for 1 h at 800 °C. The nature of the healing reactions was studied experimentally and found to be in accordance with the predicted complete filling of the indentation induced cracks via Rutile formation.

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