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Short Communication

# Oxidative Crack Healing in $Al_2O_3$ Composites Loaded with $Ti_2AC$ (A = Al, Sn) Repair Fillers

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**Abstract**

**Crack healing of alumina composites loaded with 5, 10, and 20 vol% $Ti_2AC$ (A = Al or Sn) MAX phase was investigated. Surface cracks were prepared by means of indent loading and the modulus of rupture was measured on virgin, indented, and healed specimens. The MAX phase particles serve as repair filler which reacts with oxygen penetrating along a surface crack and filling disrupted crack surfaces with the oxidation reaction products. After annealing for 3 h composites loaded with 20 vol% $Ti_2AlC$ showed full recovery at a healing temperature of approximately 900 °C, whereas lower temperatures of 700 °C were observed for specimens loaded with 10 and 20 vol% $Ti_2SnC$. The enhanced healing response of $Ti_2AC$-loaded composites containing Sn instead of Al on the A-position offers high potential for providing crack healing capability to ceramic matrix composites applied at moderate temperatures below 1000 °C.**

*Keywords: MAX phase composites, crack healing, repair filler, alumina, oxidation*

## I. Introduction

Engineering ceramics able to repair cracks upon heat treatment have gained increasing attention[1,2]. Recovery of mechanical properties depleted by overloading, slow crack growth, or thermal shock damage may offer high potential for improving the reliability and prolonging the lifetime of ceramic components subjected to mechanical loading at elevated temperatures. Crack healing behaviour of $Al_2O_3$ was observed at temperatures exceeding 1400 °C where sintering phenomena driven by the reduction of surface energy may trigger perturbation and closure of pores and cracks[3]. Significantly lower healing temperatures ≤ 1200 °C were achieved by loading $Al_2O_3$ with SiC particles and whiskers that may undergo oxidation in near-surface cracks thereby filling the crack space with $SiO_2$-based oxidation products[4–7]. Different parameters affecting the healing ability were investigated including phase composition, atmosphere, e.g. oxygen partial pressure, crack dimension as well as stress[2]. For example, a 100 μm surface crack prepared in $Al_2O_3$ composites loaded with 20 vol% SiC-whiskers could be completely recovered upon annealing in air at 1200 °C for 1 h[5]. Healing temperatures < 1000 °C, however, require repair fillers with higher reactivity than SiC.

MAX phases are ternary nitrides and carbides, with the general formula $M_{n+1}AX_n$ (n = 1 to 3), where M is a transition metal, A is an A group element, and X is either carbon or nitrogen[8]. Owing to the stronger M-X bonds and weaker M-A bonds associated with the nanolayered nature of the structure, MAX phases possess a unique combination of metal and ceramic properties. For example, they are resistant to oxidation and corrosion, elastically stiff, but at the same time, they also demonstrate high thermal and electrical conductivities and superior machinability[9]. Recent work has shown that MAX phases such as $Ti_3AlC_2$, $Ti_2AlC$ and $Cr_2AlC$ possess an interesting crack healing ability[10–12]. Cracks with a length of 7 mm and a width of 5 μm in $Ti_3AlC_2$ could be fully healed after heat treatment at 1100 °C for 2 h in air. Superior healing capability observed on $Ti_2AlC$ and $Cr_2AlC$ ceramics was attributed to the formation of adhesive $Al_2O_3$ filling the space between the disrupted crack surfaces. Furthermore, repeatable crack healing was demonstrated on $Ti_2AlC$, indicating that MAX phases offer a multiple crack-healing ability.

We have reported on the oxidation behaviour of $Ti_2Al_{(1-x)}Sn_xC$ MAX phases solid solution[13]. It was found that for a reasonable healing period of a few hours the oxidation temperature of A elements decreased from $Ti_2AlC$ to $Ti_2SnC$ from 900 °C to 460 °C. Accelerated crack healing was attributed to the higher mobility of Sn compared to Al (or Si) on the A position in the $Ti_2AC$ crystal structure, which may be favourable to promote crack healing at lower temperatures. Furthermore, MAX phase particles may serve as repair filler providing crack healing capability when dispersed in a ceramic matrix composite. It is the aim of the present work to explore oxidation-induced crack healing behaviour of $Al_2O_3$ composite loaded with $Ti_2AlC$ or $Ti_2SnC$, respectively. Composite specimens with various repair filler loading from 5, 10, and 20 vol% were prepared. Strength recovery of specimens containing indent surface cracks was analyzed for different healing temperatures.

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## II. Experimental Procedure

Alumina composites were prepared from high-purity (> 99.99 %) $Al_2O_3$ powder (AKP-53, Sumitomo Chemical Co., Ltd, Japan) with a mean particle size $d_{(0.5)} \approx 0.1 \sim 0.3\ \mu m$. $Ti_2AlC$ (> 90 %) (Kanthal, Sandvik Materials Technology GmbH, Mörfelden-Walldorf, Germany) with $d_{(0.5)} \approx 7\ \mu m$ and $Ti_2SnC$ $d_{(0.5)} \approx 5\ \mu m$ served as repair filler. $Ti_2SnC$ was synthesized from powder mixtures of Ti (4.5 μm, 99.4 %), Sn (2 μm, 99.4 %), and TiC (2 μm, 99 % purity) with a molar composition corresponding to Ti-Sn-0.9TiC. The powder mixture was annealed under vacuum for 1 h at 1200 °C. For detailed description of the synthesis see[13]. $Al_2O_3/Ti_2AC$ powder mixtures with MAX phase repair filler loading of 5, 10, and 20 vol% were thoroughly mixed for 24 h in a Turbula mixer (WAB, Basel, Switzerland). Rectangular-shaped specimens with the dimensions 50 × 50 × 5 $mm^3$ were cold-isostatic-pressed, with application of an isostatic pressure of 180 MPa. The specimens were placed in a graphite container coated with BN and pressureless-sintered at 1300 °C – 1350 °C for 4 h under vacuum atmosphere (Thermal Technology Inc., USA), with application of a heating rate of 15 K/min. No indication of thermal decomposition of either $Ti_2AlC$ or $Ti_2SnC$ was found by means of XRD. Small fractions of $Ti_3AlC_2$ and metallic Sn observed in the sintered composites resulted from the starting materials which contained approximately 10 vol% $Ti_3AlC_2$ and 4 vol% Sn, respectively.

After grinding and polishing to 1 μm surface finish, rectangular bars measuring 2.5 × 2.0 × 27 $mm^3$ were cut. Surface cracks were generated in the centre of polished bar specimens by means of Vickers' indentation (Zwick, Ulm, Germany), with the application of different loads ranging from 25 to 100 N for 10 s. Fracture toughness was derived from three-point-bend loading of the indented samples according to [14] (indentation load, rupture stress and Young's modulus were measured experimentally and a calibration constant of 0.59 was applied, respectively)[14]. Since fracture toughness of the alumina/MAX phase composites varies with MAX phase loading fraction (e.g. toughness increased with increasing repair filler loading), different indentation loads were applied to prepare similar crack lengths in all specimens. The indented specimens were annealed in ambient air atmosphere at temperatures ranging from 500 to 1100 °C for a constant period of 3 h. The phase composition before and after heat treatment was analyzed by means of X-ray diffraction (XRD) (Kristalloflex, Siemens AG, Mannheim, Germany) operating with monochromated Cu-$K_\alpha$ radiation. Oxidation reaction products filling the crack space were analyzed with scanning electron microscopy (SEM, Quanta 200, FEI, Eindhoven, Netherlands) coupled with an energy-dispersive X-ray spectrometer (EDS).

Strength recovery of the annealed specimens was derived from three-point-bending loading experiments (Instron 4204, Instron Corp., Canton, MA) applying a crosshead speed of 1 mm/min. The degree of strength recovery $\sigma_{heal}/\sigma_{virgin}$ was represented by the ratio of the modulus of rupture determined after healing to the modulus of rupture measured on the virgin sample (e.g. prior to indentation). If no healing occurred, e.g. at room temperature, $\sigma_{heal}$ is equivalent to the value of the indented specimen, $\sigma_{indent}$. For full recovery of indent crack length $\sigma_{heal}/\sigma_{virgin} \rightarrow 1$. Higher values than 1 indicate strengthening by healing and the material may attain a modulus of rupture even higher than that of the virgin material.

## III. Results and Discussion

### *(1) Repair-filler-loaded composite microstructure*

The sintered alumina/MAX phase composites were characterized by a homogeneous microstructure. Density measurements of the sintered materials according to the Archimedean principle, however, showed the fractional density to be limited to approximately 0.9. Without applying external load, full density was not achieved upon pressureless sintering owing to limitation of the sintering temperature in order to avoid thermally induced decomposition of the MAX phase repair fillers[9, 15]. Furthermore, transient stresses generated by rigid (e.g. non-sintering) repair filler particles upon alumina matrix shrinkage are reported to cause retardation of the densification rate[16]. Fig. 1 shows typical microstructures observed on the composites loaded with 10 vol% and 20 vol% $Ti_2AlC$, respectively.

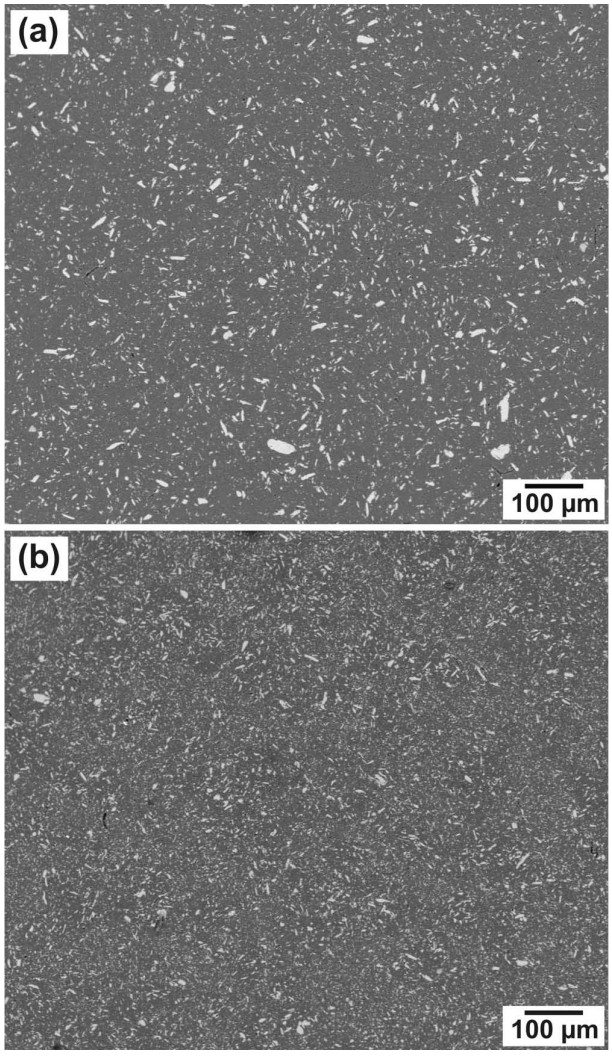


**Fig. 1:** Microstructures of $Al_2O_3$ composites after sintering at 1350 °C for 4 h loaded with (a) 10 vol%, (b) 20 vol% repair filler $Ti_2AlC$.

**Table 1:** Microstructure and modulus of rupture of alumina/MAX phase composites.

| | $Al_2O_3$ | + $Ti_2AlC$ | | | + $Ti_2SnC$ | | |
|---|---|---|---|---|---|---|---|
| Repair filler fraction $f$ [vol%] | 0 | 5 | 10 | 20 | 5 | 10 | 20 |
| Fractional sintered density | 0.93 | 0.90 | 0.92 | 0.85 | 0.89 | 0.94 | 0.89 |
| Indent crack length, $2a$ [μm] | 385 ± 11 | 395.5 ± 15 | 328 ± 12 | 264 ± 33 | 329 ± 23 | 312.3 ± 9 | 305 ± 35 |
| Repair filler particle size, $d_{par}$ [μm] | - | 5.5 ± 3 | 8.5 ± 4 | 12.5 ± 6 | 6.2 ± 3.5 | 9.3 ± 5 | 11.2 ± 5 |
| Interparticle distance, $\lambda$ [μm] | - | 12.0 | 14.7 | 17.2 | 13.5 | 16.1 | 15.4 |
| Fracture toughness, $K_{Ic}$ [MPam$^{1/2}$] | 3.2 | 3.5 | 2.7 | 3.3 | 3.7 | 3.9 | 3.6 |
| Modulus of rupture, $\sigma_{virgin}$ [MPa] | 386 ± 15 | 398 ± 23 | 340 ± 20 | 300 ± 24 | 240 ± 23 | 210 ± 26 | 200 ± 19 |
| Modulus of rupture, $\sigma_{indent}$ [MPa] | 135 ± 18 | 156 ± 5 | 106 ± 7 | 137 ± 11 | 190 ± 4 | 169 ± 12 | 168 ± 4 |

The elongated repair filler particles are homogeneously distributed in the alumina matrix. Analysis of repair filler particle size from the micrographs revealed that the particle size rose with increasing repair filler volume fraction, Table 1. The increase of the MAX phase particle size might originate from agglomeration in the starting powder mixtures as a result of mixing and milling. Low-shear conditions tend to enhance segregation and encourage agglomerate formation and growth over prolonged mixing of 24 h[17]. Calculation of the mean interparticle distance $\lambda$ between the dispersed repair filler particles[18]

$$\frac{\lambda}{d_{par}} = \left(\frac{\pi}{6f_p}\right)^{1/3} \quad (1)$$

resulted in $\lambda$-values ranging from 12 to 17 μm. For the case of a constant repair filler particle size $d_{par}$, Eq. (1) indicates that the interparticle distance $\lambda$ should decrease when the composite is loaded with higher filler volume fraction. An increasing particle size, however, counterbalances the volume change, resulting in larger interparticle distances with increasing filler loading fraction.

Indent cracks were prepared on the polished surface of the sintered specimens to generate surface cracks of controlled length and crack opening. Although the indentation load was varied carefully to account for variations of toughness with filler loading, an appreciable variance of crack length is observed with most crack lengths $2a$ ranging from 300 – 320 μm. Except for the specimen loaded with only 5 vol% $Ti_2AlC$, modulus of rupture measurements on indent-free specimens show a tendency of strength reduction with increasing repair filler loading. While reduction of virgin strength $\sigma_{virgin}$ is more pronounced on the $Ti_2SnC$-compared to the $Ti_2AlC$-loaded composites, respectively, a reverse behaviour of strength $\sigma_{indent}$ may be seen after indentation.

### *(2) Strength recovery*

Dispersion of repair filler particles into $Al_2O_3$ matrix composites triggered crack healing upon annealing treatment in air atmosphere. Oxygen may penetrate into the open crack wake and may react with repair filler particles. When the volume of oxide exceeds the volume of the pristine material, volume expansion induced by defect surface oxidation can effectively fill the defects[19]. Analysis of crack-filling products indicate that crack healing is attributed to preferred formation of oxidation products of the A-element at low oxygen activity

$$Ti_2AlC + 0.75\ O_2 \rightarrow Ti_2C + 0.5\ Al_2O_3 \qquad \Delta V/V_{Ti_2AlC} = +12\ \% \quad (2a)$$

$$Ti_2SnC + O_2 \rightarrow Ti_2C + SnO_2 \qquad \Delta V/V_{Ti_2SnC} = +29\ \% \quad (2b)$$

which is associated with a molar volume expansion factor ranging from ~ 12 % of $Ti_2AlC$ to ~ 29 % in $Ti_2SnC$[13]. XRD of the oxidation products formed on bulk composite specimens where oxygen activity is high revealed rutile-$TiO_2$ and α-$Al_2O_3$ as major products on $Ti_2AlC$-based composites and $TiO_2$ and $SnO_2$ as well as a small amount of Sn on $Ti_2SnC$-loaded alumina composites, respectively. Thus, at high oxygen activity a stoichiometric reaction may occur

$$Ti_2AlC + 3.75\ O_2 \rightarrow 2\ TiO_2 + 0.5\ Al_2O_3 + CO_2 \qquad \Delta V/V_{Ti_2AlC} = +53\ \% \quad (3a)$$

$$Ti_2SnC + 4\ O_2 \rightarrow 2\ TiO_2 + Sn_2O_2 + CO_2 \qquad \Delta V/V_{Ti_2SnC} = +76\ \% \quad (3b)$$

resulting in even more pronounced specific volume expansion of the oxidation reaction products compared to the repair fillers. For the oxidation reactions to occur, local oxygen partial pressure at the reaction site, e.g. the crack surface, must exceed a critical threshold[20] in order to provide sufficient oxidant activity for MAX phase oxidation. While small crack openings might prohibit rapid vapour and surface transport of oxygen, matrix porosity (as was the case in the pressureless-sintered composites with a fractional density ~ 0.9) might facilitate oxygen transport. We found that indent cracks up to approximately $a < 200$ μm were almost completely filled with oxidation products, Fig. 2.

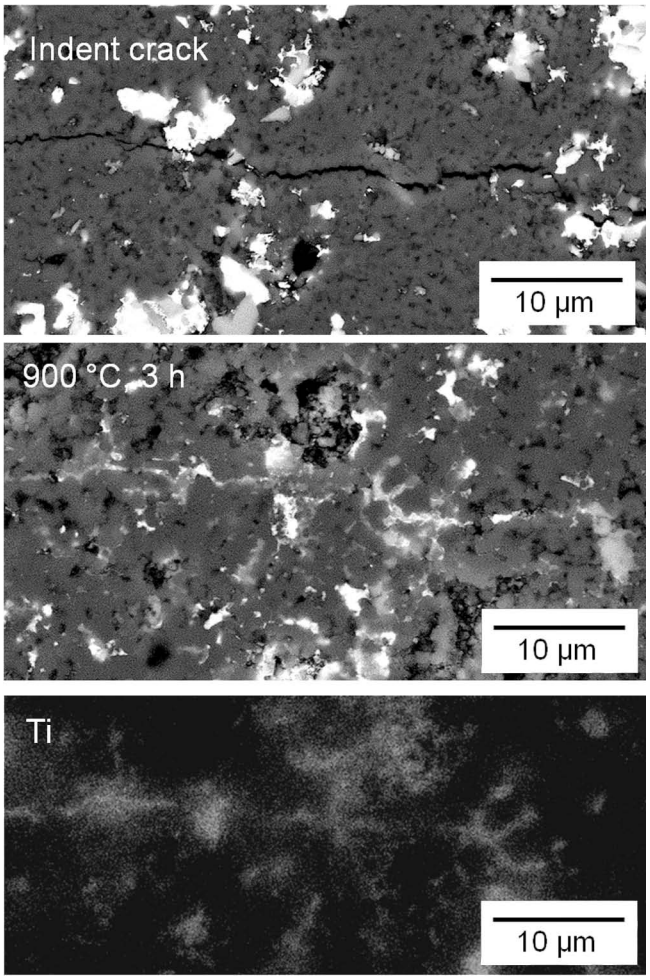


**Fig. 2:** SEM micrograph of an indent crack on the surface of $Ti_2SnC$-loaded (20 vol%) alumina matrix composite a) before and b) after annealing in air for 3 h at 900 °C and c) Ti-mapping.

Compared to the repair-filler-free alumina matrix material, a pronounced strength recovery was observed after isothermal annealing for 3 h. Fig. 3 shows the temperature dependence of the healing reaction measured on alumina composite samples loaded with 10 vol% repair fillers. Compared to the filler-free alumina matrix, which exhibits a detectable healing effect only at temperatures exceeding 1000 °C, the repair-filler-loaded composites start to recover at significantly lower temperatures. In accordance with recent reports on the oxidation behaviour of single-phase $Ti_2AC$ MAX phase, a reduction of the characteristic healing temperature (at least for a healing period of 3 h) from 900 °C to less than 700 °C is observed when A-element Al is substituted with Sn[13]. The accelerated oxidation kinetics may be related to the lower cohesive energy of Sn ($E_c$ = 8.1 eV) and migration energy on the (0001) plane ($E_m$ = 0.66 eV) compared to Al ($E_c$ = 10.4 eV and $E_m$ = 0.82 eV)[21]. Furthermore, both composites show a significant decrease of the measured strength after heat treatment at 1100 °C. Such observations might be related to the rapid growth of a discontinuous outer $TiO_2$ (rutile) layer, which is poorly adhesive on the inner $\alpha$-$Al_2O_3$ layer [9]. Another aspect is the grain growth of alumina formed in the $Ti_2AlC$ MAX phase (Eq. 3a) [22] as well as abnormal grain growth of the fine-grained $Al_2O_3$ matrix as a result of thermal treatment at T > 1000 °C. From Fig. 3, a recovery of the mechanical strength in the pure alumina matrix can be observed. This effect might be related to grain growth in the matrix material.

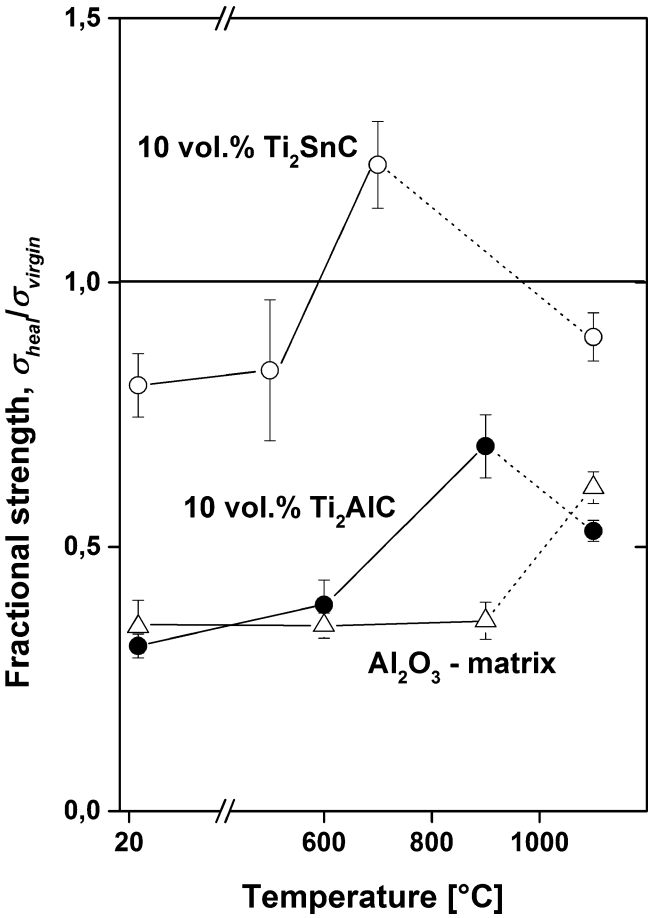


**Fig. 3:** Temperature dependence of the fractional strength of alumina composite loaded with 10 vol% repair filler after healing for 3 h.

Fig. 4 shows the variation of fractional healing strength versus variation of the repair filler volume fraction after isothermal annealing for 3 . Although the $Ti_2SnC$-loaded composite was treated at 700 °C only, recovery of healing strength attains an even higher level compared to the $Ti_2AlC$-containing specimen annealed at 900 °C. Furthermore, a minimum repair filler volume fraction seems to be necessary for effective healing to proceed. A repair filler loading of 10 vol% was sufficient to attain full recovery in $Ti_2SnC$ composites, whereas above this value a plateau is reached with no further significant increase of fractional strength. In contrast 20 vol% were required in the $Ti_2AlC$ composites to attain full strength recovery. As the repair filler size increases with the filler content in both composite systems (Table 1), the reactive surface for oxidation-induced healing reactions is slightly constrained. Therefore a significant decrease of the main particle size might offer high potential to decrease the minimum repair filler content for full strength recovery reactions. Since only minor differences were observed on the mean interparticle distance and the porosity, oxygen transport conditions may be assumed to be quite similar in both composite microstructures. Accelerated oxidation reaction and larger volume expansion in the system loaded with $Ti_2SnC$ repair filler suggest excellent potential for crack healing in composite materials.

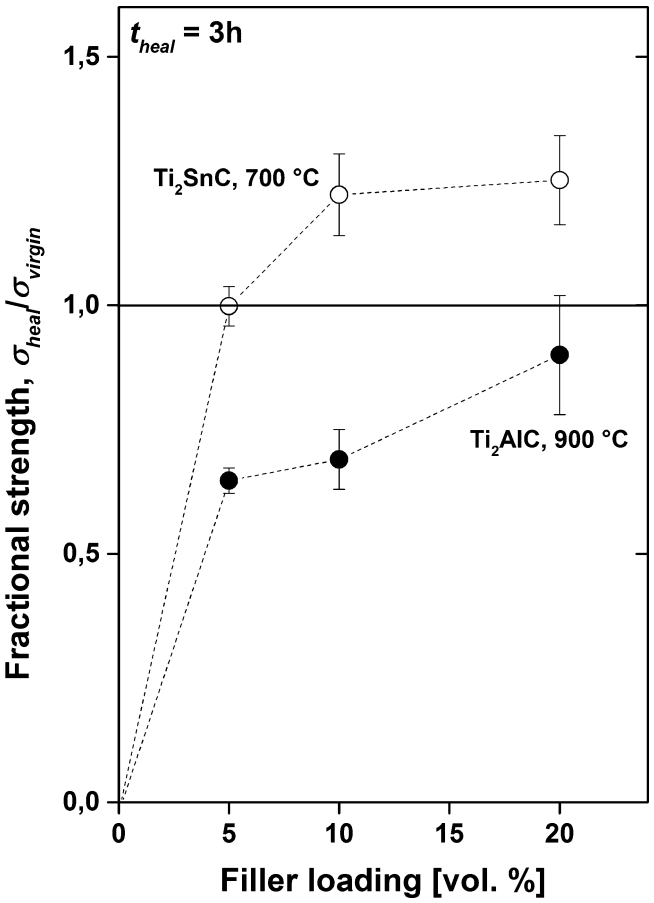


**Fig. 4 :** Filler loading dependence of the fractional strength of alumina composite after healing for 3 h at 900 °C ($Ti_2AlC$) and at 700 °C ($Ti_2SnC$).

## IV. Conclusions

It was demonstrated that alumina matrix composites loaded with MAX phase repair filler exhibit crack healing behaviour at temperatures below 1000 °C. Filling of surface cracks by oxidation products of $Ti_2AlC$ and $Ti_2SnC$ gives rise to recovery of initial strength. Our results indicate that occupation of the A-element position by Sn offers significantly higher potential for crack healing in alumina-based composite materials with repair temperatures as low as 700 °C compared to 900 °C for Al. Both material systems show significantly higher potential for crack healing reactions at healing temperatures < 1000 °C, when compared to SiC repair fillers.

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