

# METHODOLOGY TO EVALUATE AVAILABILITY OF SELF-HEALING AGENT FOR STRUCTURAL CERAMICS

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## ABSTRACT

Simple methodology to evaluate availability of self-healing agent have been established from the investigation on the relationship between oxidation behavior of self-healing agent and self-healing phenomena. The consistency of the established methodology was discussed by comparison in the lower bound of the available temperature range of mullite /  $\text{TiSi}_2$  composite. From TG / DTA analysis, the available temperature range for 10 h healing ( $T_{\text{H-10h}}^{\text{est}}$ ) was estimated to be 563 °C. On the other hand, the value of the lower bound of the available temperature range for 10 h healing ( $T_{\text{H-10h}}^{\text{exp}}$ ) was experimentally determined to be 600 °C from strength recovery tests. These values showed a good consistency. Also, the data on 1 h healing of mullite /  $\text{TiSi}_2$  and the reference data on alumina / SiC self-healing ceramics exhibited good consistency. Therefore, the proposed methodology is sufficient for evaluating the advanced healing agent.

## 1. INTRODUCTION

Oxidation induced self-healing ceramics are anticipated to apply the high temperature use with wide temperature range, for example, turbine blades of jet engine. Therefore, it is critical issue to figure out the available temperature range of healing agent. The present study aimed to derive the simple methodology to evaluate availability of self-healing agent by using mullite /  $\text{TiSi}_2$  self-healing ceramic. First, the estimated value ( $T_{\text{H}}^{\text{est}}$ ) of lower bound of the available temperature range was evaluated from the TG-DTA analysis of  $\text{TiSi}_2$  oxidation. The experimental value ( $T_{\text{H}}^{\text{exp}}$ ) of lower bound of the available temperature range was determined from the strength recovery behavior due to self-healing in mullite /  $\text{TiSi}_2$  self-healing ceramic. The consistency of the established methodology was discussed by comparison in these values.

## 2. OXIDATION BEHAVIOR OF $\text{TiSi}_2$

The value of  $T_{\text{H}}^{\text{est}}$  was estimated from the oxidation behavior of  $\text{TiSi}_2$  measured by means of TG / DTA analysis. In the analysis, the reaction heat and mass gain were measured for the oxidation of  $\text{TiSi}_2$  heating up with the constant heating rate,  $\beta$ . Figure 2(a) shows TG and DTA curves for the oxidation of  $\text{TiSi}_2$  particles at the constant heating rate of 40.0 °C / min. At the temperature which DTA curve exhibits a maximum, the TG curve is found to increase significantly. Thus, the oxidation peak temperature,  $T_p$ , was defined as the on-peak temperature of DTA curve, and

evaluated to be 619 °C when  $\beta = 40.0$  °C / min. Similar analyses were conducted for whole condition of  $\beta$ .

Figure 2(b) shows the relationship between  $T_p$  and  $\ln(\beta/T_p^2)$  for  $\text{TiSi}_2$  oxidation with the relationship for the oxidations of the other self-healing agent, where the value of  $\ln(\beta/T_p^2)$  as the vertical axis corresponds to the reaction rate constant according to Kissinger-Sunase-Akahira equation [1]. Thus, the righter plot means that arbitrary oxidation rate exhibits at lower temperature. From the figure, it is confirmed that when  $\text{TiSi}_2$  is employed as healing agent, the self-healing ceramics must exhibit the available self-healing at lowest temperature compared to the other self-healing ceramics. Osada et al. [2] reported the healing rate, corresponding to the inverse of the minimum healing time to enable to heal the pre-crack in alumina / SiC self-healing ceramic, as functions of the healed temperature,  $T_H$ , and the oxygen partial pressure,  $P_{O_2}$ , in the surrounded atmosphere as following equation;

$$\frac{1}{t_{H\min}} = 6.95 \times 10^5 \exp\left(\frac{-4.65 \times 10^4}{T_H}\right) P_{O_2}^{0.835}$$

From the equation and the relationship for the SiC oxidation shown in Figure 2(b), the values of  $\ln(\beta/T_p^2)$  can be evaluated to be -15.0 and -13.0 as the minimum healing times are 10.0 h and 1.00 h, respectively. Assuming that the self-healing rate can be simply determined from the oxidation rate of the healing agent, one can obtain the value of  $T_H^{\text{est}}$  for the self-healing ceramic containing the respective healing agent from the relationship of the oxidation of the respective healing agent shown in Figure 2(b), i.e., the values of  $T_H^{\text{est}}$  for 1.00 and 10.0 h are the equal to the values of  $T_p$  at which these relationships intersect with the horizontal lines that  $\ln(\beta/T_p^2) = -13.0$  and -15.0, respectively. Consequently, the self-healing ceramics containing  $\text{TiSi}_2$  particles as healing agent can be estimated to exhibit  $T_{H-1h}^{\text{est}}$  of 563 °C and  $T_{H-10h}^{\text{est}}$  of 577 °C.

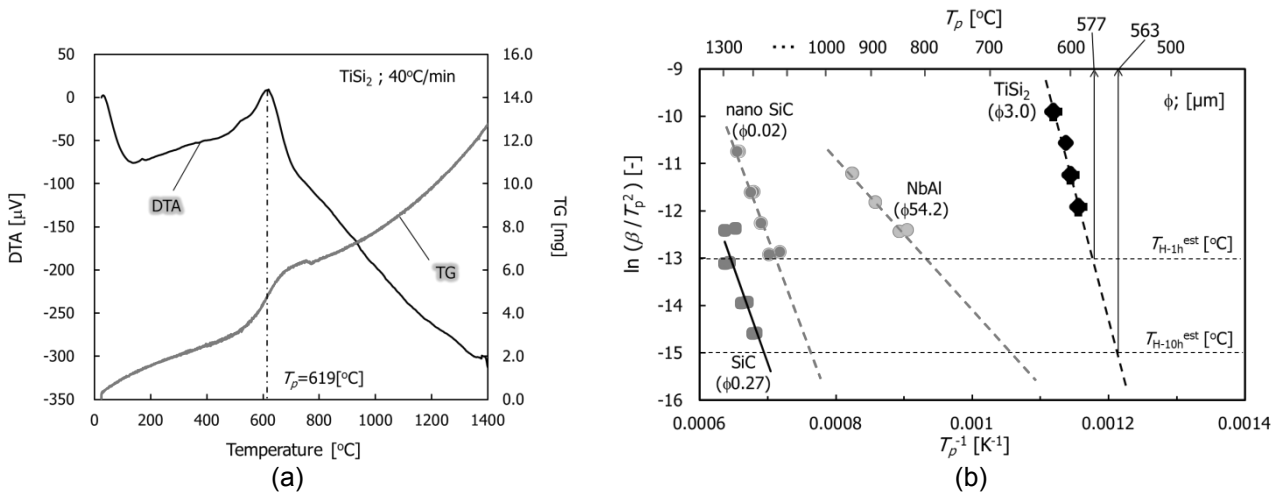


Figure 1 (a) : TG and DTA curves for the oxidation of  $\text{TiSi}_2$  at the constant heating rate of 40 °C/min, (b) : Kissinger plots of oxidations of  $\text{TiSi}_2$ , SiC, nano-SiC and NbAl.

### 3. STRENGTH RECOVERY BEHAVIOR OF MULLITE/ $\text{TiSi}_2$ COMPOSITE

The lower bound of the available temperature region,  $T_H^{\text{exp}}$ , was experimentally determined from the strength recovery behavior of mullite/  $\text{TiSi}_2$  composite. The strength recovery rate was evaluated from the strength of the specimen healed at several temperatures (400-1200 °C) for 1 and 10 h after cracked. The value of  $T_H^{\text{exp}}$

was determined to be the lowest temperature at which the strength of crack-healed specimen was recovered up to the strength of non-cracked specimen.

The specimen used for strength recovery tests was pressless sintered Mullite matrix composite containing 15 vol%  $\text{TiSi}_2$  particles as a self-healing agent. The dimension of the test rectangular bar specimen was  $4 \times 3 \times 22 \text{ mm}^3$ . The specimens were healed at temperatures from  $400 \text{ }^\circ\text{C}$  to  $1200 \text{ }^\circ\text{C}$  for 1 and 10 h after cracked at the center of the specimens by a Vickers indentation, where the indentation pre-crack had a surface length of  $100 \text{ }\mu\text{m}$ . The strength of the specimens were measured by three-point bending with span of  $16 \text{ mm}$  at room temperature.

Figure 2 shows the strength recovery rate of the mullite /  $\text{TiSi}_2$  composites healed at several temperatures for 1 h (open and closed diamonds), with that of alumina / SiC composite (closed square). The mullite /  $\text{TiSi}_2$  composites with pre-crack had the strength of  $\sim 113 \text{ MPa}$ . The composites healed at temperatures between  $600 \text{ }^\circ\text{C}$  and  $1000 \text{ }^\circ\text{C}$  for 1 h and 10 h had the strength  $\sim 183 \text{ MPa}$  and the composite without pre-crack also has almost same strength. Thus, the strength recovery rates of 0 % and 100 % for the mullite /  $\text{TiSi}_2$  composites correspond to the  $113 \text{ MPa}$  and  $183 \text{ MPa}$ , respectively. Since the strength recovery rates at temperatures below  $500 \text{ }^\circ\text{C}$  do not reach 100 %, the value of  $T_{H-1h}^{\text{exp}}$  was determined to be  $600 \text{ }^\circ\text{C}$ . Also the value of  $T_{H-10h}^{\text{exp}}$  was determined to be  $600 \text{ }^\circ\text{C}$ . No difference between  $T_{H-1h}^{\text{exp}}$  and  $T_{H-10h}^{\text{exp}}$  is directly influenced by the small difference between  $T_{H-1h}^{\text{est}}$  and  $T_{H-10h}^{\text{est}}$ .

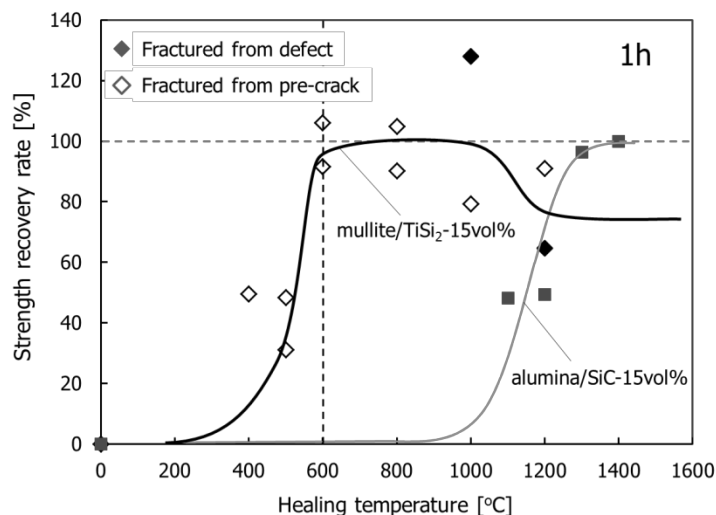


Figure 2 : The strength recovery rate of the mullite /  $\text{TiSi}_2$  composites healed at several temperatures for 1h with that of alumina / SiC composite.

#### 4. DISCUSSION

Figure 3 shows the consistency between the values of  $T_H^{\text{est}}$  and  $T_H^{\text{exp}}$  for the self-healing in mullite /  $\text{TiSi}_2$  composite with some examples [3], [4]. The plots in this figure indicate  $T_H^{\text{exp}}$  for several self-healing ceramics and the attached bars demonstrate the available temperature range of these ceramics, i.e. the upper and lower bounds of the bars indicate the heat resistance limit-temperature and  $T_H^{\text{exp}}$ , respectively. The direct proportion line means the value of  $T_H^{\text{est}}$  is in perfect agreement with the value of  $T_H^{\text{exp}}$ . Every plot shows good agreement with this line so that one could argue that there is good consistency between estimation and experimental value of lower limit temperature, regardless of self-healing agent and healing time.

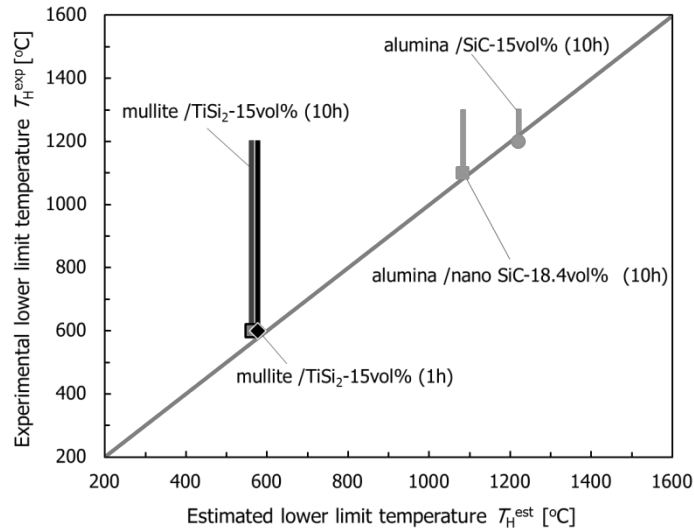


Figure 3: The consistency between the values of  $T_H^{est}$  and  $T_H^{exp}$  for the self-healing in mullite / TiSi<sub>2</sub> composite with those in alumina / SiC composite and alumina / nanometer-sized SiC composite

## 5. CONCLUSIONS

The obtained results show that the proposed method is sufficient to evaluate availability of self-healing agent. Therefore, using this method, one can easily estimate whether the new self-healing ceramics containing new healing agent is suitable to the corresponded applications.

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