Effects of chemical properties of healing agents on self-healing ability of oxidation induced self-healing ceramics

酸化誘起型自己治癒セラミックスの自己治癒性に及ぼす治癒発現物質の化学的特性の影響

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The present study aims to clarify the correlation between the chemical reaction of healing agents and mechanical strength recovery of oxidation induced self-healing ceramics. Based on the obtained results, material design strategy for oxidation induced self-healing ceramics is proposed.

The oxidation-induced self-healing ceramics discussed in the study are the potential candidates for advanced high temperature structural materials. The oxidation-induced self-healing is an autonomous function enabling composites to fully restore mechanical properties in situ. This process is induced by the high temperature oxidation of non-oxide particles, called healing agents, that are embedded in oxide ceramics. Owing to this remarkable property, the ceramic matrix composites are able to avoid catastrophic failure and actively maintain their structural integrity during operation. Despite the fact that high temperature structural materials have various operating temperature ranges, the temperature range of self-healing ceramics in which the desired healing reaction can be observed is quite limited.

This temperature range, called the healing temperature range (T_{H}), is directly affected by the chemical properties of the healing agent. Methodologies for evaluating the upper and lower limits of the healing temperature range (T_{H}) were proposed by clarifying the effects of the chemical properties of the healing agent on self-healing behaviour. Additional practical methodologies for customizing healing agents (the use of cation and interface design) were proposed based on the discussion of the relationships between strength recovery behaviour and micro-structure changes in self-healing ceramics.

By integrating the proposed methodologies, an advanced self-healing ceramic that shows the desired self-healing behaviour under the specific operating conditions of high temperature structural materials can be designed. The conclusion of each chapter is briefly summarized below.

Chapter 1 Introduction

The chapter clearly described the impacts of the study on both scientific and industrial fields. Current development status and the practical issues of high temperature structural materials used in transportation were investigated, and social requirements in the materials development were discussed. The promise of implementing self-healing ceramics in replacement for their classical counterparts was also described. To expand the study's scientific context, previously proposed self-healing ceramics were organized using the research and development information of self-healing material. The current issues in the field of self-healing ceramics were extracted from those discussions, and the purpose of the study was described.

Chapter 2 Methodology for Evaluating Healing Agents for Oxidation-Induced Self-Healing Ceramics

The chapter dealt with the methodology for evaluating potential healing agents for oxidation-induced self-healing ceramics. The theoretical frame work for predicting the healing ability of non-oxides was presented based on thermodynamic analysis. The methodology for estimating the lower limit temperature of the healing temperature range ($T_{\mathrm{H\text{-}low}}$) was proposed by quantitatively evaluating of the relationship between the oxidation behaviour of the healing agents and the strength recovery behaviour of self-healing ceramics. The estimated value of the lower limit ($T_{H\text{-}low}^{est}$) was determined using thermogravimetric analysis, and the experimental value ($T_{H\text{-}low}^{exp}$) was derived from strength recovery tests of self-healing ceramics. The estimated value for $T_{H\text{-}low}^{est}$ was close to the experimental value $T_{H\text{-}low}^{exp}$ in the cases of the alumina/SiC composite and porous mullite/$TiSi_2$ composite. From the above studies, it was shown that the proposed methodology was sufficient for evaluating the self-healing potential of the healing agents.

Chapter 3 Effect of Cation in Healing Agents on Self-Healing Behaviour

In this chapter, the effect of cation in healing agents on self-healing behaviour was studied. The effect was clarified through the experiment on strength recovery behaviour and through micro-structural observation of the alumina/TiC composite. The selection of TiC was made based on the method described in Chapter 2. The strength of the material recovered to its original level within 1h by annealing at 800°C. Excess outward diffusion of Ti cation was observed at 1000°C. This result indicates that the cation could enhance the oxidation activity of the healing agent. This also shows the viability of healing agents containing Ti cation in lower temperature applications.

Chapter 4 Methodology for Evaluating the Lifespan of Self-Healing Ability

The chapter dealt with the methodology for evaluating the upper limit temperature of the healing temperature range ($T_{H\text{-}high}$). Self-healing ceramics should maintain their self-healing ability even when constantly exposed to high temperature atmospheres. In such severe conditions, healing agents embedded in the matrix can deteriorate due to inward diffusion of oxygen. It was shown that self-healing ability disappears due to internal oxidation through strength recovery tests on alumina/SiC composites aged at 1200°C for 1000h. This indicates that the lifespan of self-healing ability can be evaluated as a function of the growth rate of the internal oxidation layer. Based on this, a methodology for evaluating the upper limit temperature of the healing temperature range ($T_{H\text{-}high}$) was proposed.

Chapter 5 Interface Design Between Matrices and Crack Filling Oxides

The chapter dealt with the effects of interface conditions between matrices and crack-filling oxides on the strength recovery behaviour of self-healing ceramics. The effects were discussed based on the results of strength recovery testing of alumina/TiC composites as a function of annealing time. The strength recovery of the composite at 600°C showed an almost constant value of 50% regardless of annealing time, even though the pre-crack was fully filled with formed TiO_2. The intermediate compound Al_2TiO_5 was not detected below 600°C, where the strength recovery value was saturated. Those results imply that the formation of intermediate compounds at crack-healed area plays an important role in achieving the desired bonding of the interface between the matrix and the formed oxide, which results in the complete strength recovery of the self-healing ceramic. A methodology was proposed on the basis of thermodynamics to evaluate oxide matrices and to determine which compounds can attain the desired bonding of the interface.

Chapter 6 Conclusions

This chapter concludes this study and offers suggestions for further research. In Chapters 2 and 4, methodologies for evaluating the upper and lower limits of the healing temperature range (T_H) were proposed. Additional practical methodologies for customizing healing agents utilizing cation and interface design are described in Chapters 3 and 5. By integrating those proposed methods, an advanced self-healing ceramic can be designed that will demonstrate the desired self-healing under the specific operating conditions of high temperature structural materials. Throughout the study, fundamental design strategies for oxidation-induced self-healing ceramics are proposed.