A CONCEPTUAL STUDY INTO THE POTENTIAL OF MAX-PHASE CERAMICS FOR SELF-HEALING OF CRACK DAMAGE

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Keywords: MAX Phase, crack-healing, high temperature oxidation

ABSTRACT

The reduction of maintenance and replacement work costs is an important driving force in the development of high temperature materials (T>800 °C) that can autonomously heal damage as a result of local cracks. In recent years some potential routes involving the addition of sacrificial particles have been identified, yet these systems have the drawback of reduced initial properties and being capable of healing cracks only once. Hence there is a need for high temperature materials with high initial properties and an ability to heal cracks several times.

Ti_2AlC, being a member of the MAX-Phase ceramics family has shown an unusual ability to heal cracks multiple times through selective oxidation of Al, while maintaining its salient mechanical properties [1]. It is to be expected that other compounds of the $M_{n+1}AX_n$ family, where M is a transition metal, A an element from groups 13 or 14 and X either Carbon or Nitrogen combining characteristics of metals and ceramics, may also show self-healing abilities.

In this work MAX phases known to date (approx. 85) have been evaluated to establish a group of potential compounds expected to be promising applicants of (multiple) crack-healing. To this end, their thermodynamics and material transport at elevated temperatures determining the selective oxidation kinetics and crack filling potential have been considered.

MAX phases with Al and Si are of special interest since the oxides of these A elements have been shown to act successfully as healing agents [2, 3]. While not having been explored, MAX phases which in combination with the oxidation of the M element form a single ternary oxide may also offer attractive self-healing potential.

MAX phases that show an above average potential for self-healing have been identified, in order to guide the experimental research into the wider exploration of MAX phase ceramics for intrinsic high temperature self-healing ceramics.

1. INTRODUCTION

Throughout time materials have been designed and modified in accordance with ‘the damage prevention principle’ [4] meant to delay damage, such as cracks, but not reacting to it. In recent years the research on materials capable of autonomous crack healing has yielded multiple mechanisms, such as addition of sacrificial particles and use of bacteria in concrete. Within the high temperature materials (say >800 °C) a young class of ceramics, the MAX phase ceramics have shown even multiple self-healing potential through selective oxidation. These composites with the nomenclature $M_{n+1}AX_n$, where M is an early transition metal, A an element of the groups IIIA and IVA and X either C and/or N, combine high thermal and electrical conductivity with machinability, corrosion resistance and high stiffness, amongst others.
Based on (multiple) self-healing results achieved with Ti_2AlC a theoretical investigation of further potential compounds is performed to narrow the field of about 85 known MAX phases.

2. POTENTIAL SELF-HEALING MAX PHASES

Generally, healing by selective oxidation relies on the properties of the formed oxide as well as on the reaction kinetics and thermodynamics. Promising healing agents have been shown to be the oxides of the A element, e.g. Al_2O_3 and SiO_2 [1, 5], partially due to higher atom mobility within the layered hexagonal structure.

To limit the scope of the investigation the sum of known compounds is restricted to $M_{n+1}AX_n$ phases with n equals to =1, 2 or 3. No modified compounds such as $Ti_2Al(Si)C$ will be analysed. As the oxidation behaviour of many MAX phase materials has not been investigated yet, thermodynamic and kinetic data is used to evaluate the potential for self-healing such as: Gibbs free energy of oxide formation, atom mobility, coefficient of thermal expansion, etc..

Table 1 : $M_{n+1}AX_n$ (n=1, 2 to 3) Phase Ceramics

M\A	Al	Si	Ge	Ga	As	P	S	In	Sn	Tl	Pb	Cd	
Ti	Ti_2AlC Ti_2AlN Ti_3AlC2 Ti_4AlN3	Ti_3SiC_2 Ti_4SiC_3 Ti_2SiC Ti5SiC4	Ti_2GeC Ti_3GeC_2 Ti_4GeC_3	Ti_2GaC Ti_2GaN Ti_4GaC_3	Ti_2AsC	Ti_2PC	Ti_2SC	Ti2InC Ti2InN	Ti_2SnC Ti_3SnC_2 Ti_7SnC_6	Ti_2TlC	Ti_2PbC	Ti_2CdC	25
Cr	Cr_2AlC	Cr_2SiC Cr_3SiC_2	Cr_2GeC	Cr_2GaC Cr_2GaN		Cr_2PC	Cr_2SC						8
V	V_2AlC V_3AlC_2 V_4AlC_3	V_2SiC V_3SiC_2	V_2GeC	V_2GaC V_2GaN	V_2AsC	V_2PC	V_2SC						11
Sc	Sc_2AlC			Sc_2GaC Sc_2GaN				Sc_2InC		Sc_2TlC			5
Nb	Nb_2AlC Nb_4AlC_3	Nb_3SiC_2	Nb_2GeC	Nb_2GaC	Nb_2AsC	Nb_2PC	Nb_2SC	Nb_2InC	Nb_2SnC				10
Mo		Mo_3SiC_2		Mo_2GaC									2
Zr	Zr_2AlC Zr_2AlN	Zr3SiC2					Zr_2SC	Zr_2InC Zr_2InN	Zr_2SnC	Zr_2TlC Zr_2TlN	Zr_2PbC		9
Hf	Hf_2AlC Hf_2AlN	Hf_3SiC_2					Hf_2SC	Hf_2InC	Hf_2SnC Hf_2SnN	Hf_2TlC	Hf_2PbC		9
Ta	Ta_2AlC Ta_3AlC_2 Ta_4AlC_3 Ta_6AlC_5	Ta_3SiC_2		Ta_2GaC									6
	19	12	6	12	3	4	6	7	7	5	3	1	85

Firstly, considering future high temperature applications (T>800 °C), volatile A element oxides can be excluded, such as those of As, P and S with decomposition and boiling temperatures of 315, 173 and 45 °C, respectively.

Thermodynamic evaluation of the oxidation sequence is performed by comparison of the Gibbs free energy of oxide formation per mole of O_2 in a temperature interval of 500-1700 K. The healing agent is required to have a lower (more negative) value than the competing M element, to ensure the preferential formation of the A oxide. The Gibbs free energy of formation per mole of O_2 for TiO_2 and its competing A element oxides is shown in

Figure 1. For example the oxidation of Tl exhibits much lower reaction energies in the temperature range of 500-1700 K than the formation of TiO_2, deeming it an unlikely healing agent for Ti containing MAX phases.

The competing oxidation reactions cannot only lead to mixtures (layering) of different oxidation products, but to ternary oxides with possible beneficial attributes. Analysing the Gibbs free energy of oxide formation for possible combinations between the transition metal (M), the A element and oxygen can bear insight into advanced healing agents. An example of such is the ternary oxide $ZrSiO_4$, formed between SiO_2 and ZrO_2.

Furthermore, recovery of initial properties not only depends on the healing agent itself, but on its adhesion to the original matrix. Spallation and stress induced cracking are undesirable effects dependent on lattice orientation and mismatch of thermal expansion coefficients. For example the difference between the thermal expansion coefficient of TiO_2 and that of Ti_2AlC can lead to poor adherence thus reducing the strength recovery [6].

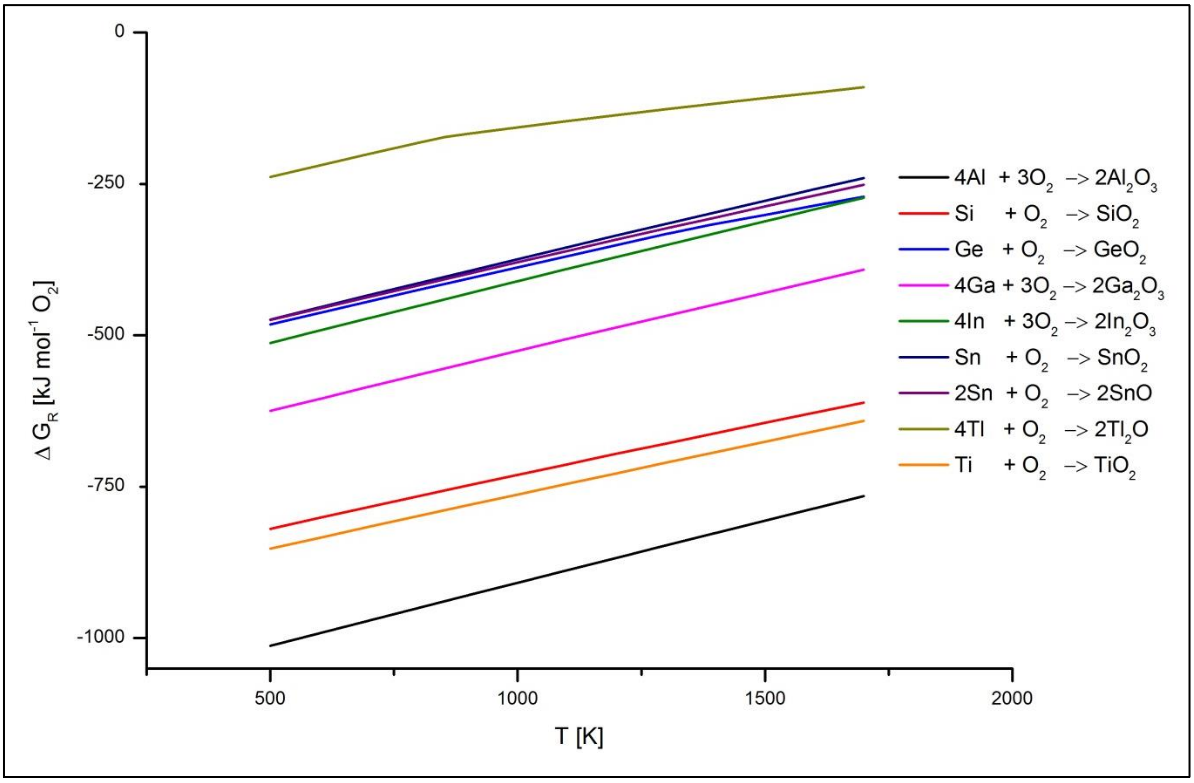

Figure 1 : Gibbs free energy of oxide formation per mole of O_2 for Ti and its associated A group elements

Based on the described factors, MAX phases with Al, Si and Ga show highest potential for crack-healing. A possible ternary oxide with favourable properties is $ZrSiO_4$, which has a low coefficient of thermal expansion and a Gibbs free energy of oxide formation between that of SiO_2 and ZrO_2. However Zr and Si containing MAX phases have yet to be synthesized. Experimental investigations into the large stable group of Al containing compounds shows great potential for development of self-healing materials.

3. CONCLUSION

Criteria to identify MAX phases that show potential for self-healing have been established, in order to guide the experimental research into the wider exploration of MAX phase ceramics for intrinsic high temperature self-healing ceramics. Thermodynamic and kinetic constraints of selective oxidation, such as Gibbs free energy, diffusivity and thermal expansion are investigated to develop a comprehensive method for the selection of ternary Carbides and Nitrides of the $M_{n+1}AX_n$ group with crack-healing ability. A first evaluation showed that MAX phases with Al, Si and Ga exhibit a high potential for crack-healing.

ACKNOWLEDGEMENTS

Financial support of the European Commissions 'Marie Curie International Training Network for Self-Healing Materials: from Concept to Market' (www.SHeMat.eu), project number 209308, is gratefully acknowledged.

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