OXIDATION INDUCED CRACK HEALING OF CR$_2$(AL,SI)C MAX PHASE CERAMIC

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ABSTRACT

The oxidation crack healing of Cr$_2$AlC and Cr$_2$(Al, Si)C was studied and compared with known healing of Ti$_2$AlC. The oxidation induced crack healing of Ti$_2$AlC is relatively fast and leads to full strength recovery, but the oxidation product contains besides $\alpha$-Al$_2$O$_3$ also undesired TiO$_2$. However, when oxidizing Cr$_2$AlC only $\alpha$-Al$_2$O$_3$ is formed, but full crack healing is relatively slow. The efficiency of the oxidation induced crack healing of Cr$_2$AlC is enhanced if Al is partially replaced by Si atoms.

1. INTRODUCTION

MAX phase materials, such as: Ti$_3$AlC$_2$ and Ti$_2$AlC, are very attractive materials in their own right as they combine desirable metallic and ceramic properties at the same time due to their atomically layered and hexagonal crystal structure. In our earlier studies [1, 2], we demonstrated that these materials possess interesting self-healing properties when exposed to high temperatures in an oxidizing environment. The recovery of mechanical strength is mainly due to the formation of higher strength $\alpha$-Al$_2$O$_3$, but also some weaker TiO$_2$ is present in the healed crack.

To avoid the formation of TiO$_2$, which is not beneficial for the adhesion between the two fracture surfaces, the crack healing of Cr$_2$AlC was explored. However, full crack healing of Cr$_2$AlC was found to be slow compared with that of Ti$_2$AlC due to the slower oxidation kinetics. To accelerate the oxidation process some of the Al atoms in the Cr$_2$AlC are to be replaced by Si atoms. Therefore, the oxidation kinetics and the composition of the oxidation product is studied for Ti$_2$AlC, Cr$_2$AlC and Cr$_2$(Al, Si)C after isothermal oxidation in synthetic dry air at temperature at 1100 °C. Finally, the crack healing performance and strength recovery of these MAX phases are compared.
2. MATERIALS AND METHODS

The oxidation kinetics of the MAX phase $\text{Ti}_2\text{AlC}$, $\text{Cr}_2\text{AlC}$ and $\text{Cr}_2(\text{Al, Si})\text{C}$ in $\text{N}_2$ with 20 vol.% $\text{O}_2$ at 1100 °C were determined with thermography analysis (TGA). The oxidation products were analysed with X-ray microanalysis and X-ray diffractometry.

Crack damage was generated with Knoop indentation in the centre of the samples with dimensions of 3x4x36 mm applying a load of 50 to 1000 N. Next, the cracks were healed at 1100 °C in air for 4 hours.

The strength of the materials before and after oxidation induced crack healing was determined by 3-point bending with a span of 30 mm and cross-head speed of 0.5 mm/min.

3. RESULTS AND DISCUSSION

Cracks in $\text{Ti}_2\text{AlC}$ can be healed relatively fast at high temperatures in an oxidizing environment. For example, for this MAX phase full crack healing and strength recovery has been observed within 1 hour at 1200 °C [2]. The healing product is mainly composed of $\alpha$-$\text{Al}_2\text{O}_3$ and some TiO$_2$. Similar experiments with $\text{Cr}_2\text{AlC}$ and $\text{Cr}_2\text{AlSiC}$ showed that the crack healing and strength recovery takes much longer time [3]. This is in agreement with the oxidation kinetics observed for these 3 MAX phases; see Figure 1. Partial replacement of Al by Si in the lattice of $\text{Cr}_2\text{AlC}$ [4] promotes significantly the formation of $\alpha$-$\text{Al}_2\text{O}_3$ and thus the crack healing.

![Figure 1: Oxidation kinetics of $\text{Ti}_2\text{AlC}$, $\text{Cr}_2\text{AlC}$ and $\text{Cr}_2(\text{Al, Si})\text{C}$ in $\text{N}_2$ with 20 vol.% $\text{O}_2$ at 1100 °C.](image-url)
Large cracks in Cr$_2$AlC, as generated with Knoop indentation, were fully healed when sufficient time was allowed for oxidation; see Figure 2. In the example presented here, a crack of about 1 mm length and 2-3 µm width was healed after 100 hours of oxidation in N$_2$ with 20 vol.% O$_2$ at 1100 °C. The crack gap is filled with $\alpha$-Al$_2$O$_3$ and some Cr$_2$AlC debris as a result of the fracturing. If the crack gap was not fully filled with $\alpha$-Al$_2$O$_3$ then the strength determined with 3-point bending was lower than the strength of the virginal material [3].

![Figure 2](image)

Figure 2: Backscattered electron images of a crack in Cr$_2$AlC healed at 1100 °C for 100 h in air. (a) A low magnification image of the cross section taken along the A-A direction; see insert (b, c and d) Enlarged images taken from the marked areas denoted as ‘1’, ‘2’ and ‘3’ in (a), respectively.

Since the time for crack healing in practical applications is usually limited, a more efficient healing is required. For Cr$_2$AlC, this can be realized by partially replacing Al by Si in the MAX phase [4]. Then the time for healing a crack is significantly reduced.

4. CONCLUSIONS

Upon exposure at high temperatures in an oxidizing environment, cracks in Ti$_2$AlC are fully healed by filling the crack gap with Al$_2$O$_3$ and TiO$_2$. However, the rutile (TiO$_2$) formed weakens the adhesion between the two fracture surfaces. Cracks in Cr$_2$AlC, on the contrary, are healed exclusively with $\alpha$-Al$_2$O$_3$, but the filling of the crack gap by oxidation proceeds much slower compared with Ti$_2$AlC. Partial replacement of Al atoms in Cr$_2$AlC with Si atoms promotes the formation of $\alpha$-Al$_2$O$_3$ and thus the crack healing.
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