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Enhanced efficiency of self-healing of Cr₂AlC

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ABSTRACT

A method for a significant improvement of the self-healing efficiency of Cr₂AlC ceramic via pre-oxidation is presented. Micro-notches were made with the focused ion beam technique on specimens with a pre-existing oxides scale followed by an oxidation healing treatment. An interesting finding is that in the former case the notches are more effectively healed by producing a dense Al₂O₃ layer than the counterpart specimens without a pre-existing scale. An explanation for this phenomenon is provided based transmission electron microscopy revealing a transition layer between Cr₂AlC and Al₂O₃ with a gradient distribution of chemical composition.

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1. Introduction

Self-healing materials have attracted considerable interest in recent years due to their potential applications in harsh environment where damage repair is rather difficult [1–3]. Some of these materials are the so-called MAX phase ceramics [4–9]. In the present work, we concentrate on the healing behavior of surface notches in Cr₂AlC *with* and *without* a pre-existing oxide scale so as to reveal the influence of these relevant conditions on the self-healing efficiency. This paper sets aside from the previous publications [9,10] that here a novel method for significant improvement of the self-healing efficiency is presented in which the oxidation rate in notches of Cr₂AlC is much faster than on the scale-protected outer surface.

2. Experiments

The initial Cr₂AlC ceramic was prepared by hot pressing of mechanically alloyed Cr, Al and C powder mixture at 1100 °C for 1 h at 30 MPa in Ar atmosphere [10,11]. Two rectangular bars are referred to as *Sample-A* and *Sample-B* to perform the notch-healing experiments *without* and *with* pre-oxidation treatment, respectively. The oxide scales were obtained on *Sample-B* surface by annealing in a furnace preheated to 1100 °C for 2 h in flowing

air. Surface notches with different sizes (width and depth) were made on the upper surface of the fresh polished *Sample-A* and the oxidized *Sample-B* by focused ion beam (FIB) milling. After FIB milling, *Sample-A* and *Sample-B* were treated at 1100 °C for 2 h.

3. Results and discussion

Fig. 1a shows an EBSD orientation map obtained from the equiaxed Cr₂AlC ceramic with the average size of about 2 μm. Fig. 1b shows a typical SEM image with back-scattered electron (BSE) contrast of the oxide scale formed on *Sample-A* surface after oxidation (healing) at 1100 °C for 2 h. The scale morphology shows a homogeneous and compact feature consisting of fine Al₂O₃ grains according to EDS elemental analysis (not shown here for the sake of brevity). The cross sections of three healed notches of different sizes in *Sample-A* are displayed in Fig. 1c. Cr₂AlC matrix and Al₂O₃ grains are in gray and dark gray contrasts, respectively, which is mainly due to the atomic number differences in BSE imaging (Z-contrast). It is clear seen in Fig. 1c that some areas on the sample surface (exactly located at the initial notches in *Sample-A*) were not fully healed. In addition, the unfilled volume increases with increasing initial notch size. Furthermore, some voids are detected at the Cr₂AlC–Al₂O₃ interface or in the middle of the healed notches (denoted by the arrows in Fig. 1c).

In order to compare the healing behavior of *Sample-A* and *Sample-B*, four FIB-made notches on the oxidized surface of *Sample-B* are shown in Fig. 2a. In contrast to the healed-notches of *Sample-A*, *Sample-B* an oxide ridge is clearly formed on each

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Fig. 1. (a) EBSD map of the initial Cr_2AlC ceramic, (b) Al_2O_3 scale and (c) BSE image of the healed-notches in the Sample-A after healing at 1100 °C for 2 h.

Fig. 2. (a) Notches on the pre-oxidized Cr_2AlC surface Sample-B; (b) top-view of the healed notches after healing at 1100 °C for 2 h; and (c) BSE images showing the healed notches.

notch site. The increment of the oxide scale thickness on the flat surface is approximately $0.3\ \mu\text{m}$, while that on the notch wall can be as large as $2.0\ \mu\text{m}$, respectively. These observations prove that the oxidation rates in notches are much faster than those on the scale-protected surface.

The oxidation kinetics of Cr_2AlC can be obtained by measuring the gain in weight as well as the scale thickness increment during annealing in hot air, with oxidation time [12–16]. Fig. 3a shows a typical cross-section TEM image of *Sample-A* indicating that the Al_2O_3 scale with an average thickness about $1.3\ \mu\text{m}$ after 2 h of oxidation at $1100\ ^\circ\text{C}$. Fig. 3b shows a high resolution TEM image of the Cr_2AlC - Al_2O_3 interface obtained from $[1\ 1\ 0]_{\text{Al}_2\text{O}_3}$ zone axis, with the Fast Fourier Transformation (FFT) of Al_2O_3 lattice in the insert. Interestingly, a transition layer approximately 5 nm thick between the matrix and the Al_2O_3 scale is detected, as shown in Fig. 3b [17]. The EDS elemental profiles shown in Fig. 3c are obtained from the line-scan across the transition layer as indicated by an arrow in Fig. 3b, which clearly reveal a transition layer.

Generally speaking, the contents of Al and O are reduced in the transition layer from oxide scale to the matrix, and simultaneously the Cr content increases gradually along that direction. The C content exhibits a small peak in the transition layer, as denoted by the arrow in Fig. 3c. In addition to the observation that Al_2O_3 dominates the oxide scale during healing, these results strongly indicate

that the transition layer is composed of Cr, Al, C, and O elements, rather than Cr-C layer. This is different with the scale formed on Cr_2AlC , i.e. the outer Al_2O_3 layer and the inner chromium carbides layer [13,14]. The transition layer with nano-scale in this work is due to the shorter healing time.

By comparing the notch-healing performance of *Sample-A* and *Sample-B*, three important take-home messages are concluded. First, the notches in *Sample-B* could be fully healed at $1100\ ^\circ\text{C}$ in air for 2 h, while those in *Sample-A* could not. Secondly, the scale growth in notches is much faster than that on a flat surface of *Sample-B*. In contrast, the oxide scale growth rates on the surface or on the notch walls are basically the same for *Sample-A*. Third, a few voids could be detected at the Cr_2AlC matrix and Al_2O_3 interface, as well as in the middle of the healed notches for both samples.

For a better clarification of the mechanisms of accelerated oxides formation and notch healing, Fig. 4 illustrates the corresponding schematic of scale growth and voids formation. It is hypothesized that the driving force of the oxides scale growth has a Coulombic origin, i.e., the O^{2-} concentrated on the oxide/gas interface and the Al^{3+} concentrated on the matrix/scale interface, as presented in Fig. 4a. The intrinsic set-up electric fields can be generated because of dipolar fields at the surface of ceramics/oxides leading to a concentration gradient as a function of the distance to the free surface [18]. With the increase of the scale thickness, the driving force will decrease and as a result the growth rate of the scale will slow down [19,20]. We propose that the oxidation for Cr_2AlC exhibits two oxidation stages, an early oxidation stage (before formation of a continuous and dense Al_2O_3 scale) followed by a second oxidation stage (after formation of a continuous and dense Al_2O_3 scale). In the early stage, the oxygen partial pressure is high enough for the simultaneously nucleation of Al_2O_3 and

Fig. 3. (a) Bright field TEM image showing the Al_2O_3 scale formed on the Cr_2AlC surface at $1100\ ^\circ\text{C}$ for 2 h. (b) TEM image of the Cr_2AlC - Al_2O_3 interface, and (c) EDS line-scan across the transition layer as indicated by an arrow in (b).

Fig. 4. Schematic illustration of the enhanced oxidation behavior of Cr_2AlC with pre-exist oxide scale: (a) localized healing in the fresh notch and (b) formation of voids due to the evaporation of Cr_2O_3 .

Cr–O oxides on the surface of Cr_2AlC (Fig. 4a). Cr_2O_3 should form preferentially since the Gibbs free energy of Cr_2O_3 is the lowest one of the listed Cr-containing oxides [18]. No Cr_2O_3 was found around the Al_2O_3 scale formed in the temperature range 900–1200 °C. The absence of Cr_2O_3 is due to evaporation above 900 °C of Cr_2O_3 formed in the early stage.

4. Conclusions

The novelty of the paper is the enhanced efficiency of self-healing of Cr_2AlC . It is shown that the oxide formation rate in notches is significantly faster than on flat surfaces. The explanation is based on a transition layer between Cr_2AlC and Al_2O_3 with a gradient distribution of chemical composition.

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