SELF-HEALING OF YTTRIUM-DOPED CR_2ALC MAX PHASE COATINGS DEPOSITED BY HIPIMS

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ABSTRACT

Self-healing materials allow for a design concept based on damage management where damage that is inflicted during operation can be healed autonomously. It has been shown that the $M_{n+1}AX_n$ phases Ti_3AlC_2, Ti_2AlC and Cr_2AlC exhibit autonomous self-healing behaviour. Cracks are filled and hence healed by oxidation products of the M and A elements in the MAX phase at high operating temperatures. After crack healing the fracture strength is recovered to the level of the virgin material.
Cr_2AlC MAX phase was shown to exhibit excellent erosion resistance and high damage tolerance. The oxide scale forming in the temperature range between 900-1200°C after different oxidation times was studied. The influence of the addition of Y on the rate of oxidation of Cr_2AlC films and on their self-healing behaviour was investigated. The aim of the ongoing research project is to assess the potential of Cr_2AlC MAX phase coatings as autonomous self-healing material by understanding the basic physical and chemical principles governing multiple crack closure to heal erosion damage.

1. INTRODUCTION

The oxidation behaviour of Cr_2AlC has been studied mainly for bulk material so far [1-3] and the oxidation mechanism is not yet fully understood. Interaction with oxygen, especially incorporation of oxygen in the initial stages of oxidation, is essential for the understanding of the oxidation mechanism and improving of the oxidation resistance of this material [4]. Systematic studies of oxygen incorporation into MAX phases are still missing in the literature. Additionally, oxygen dissolution is of importance for the design of self-healing of MAX phases, e.g. [5]. We have focused in this study on the initial stage of the oxidation of the Cr_2AlC-MAX phase synthesized as thin films by High Power Impulse Magnetron Sputtering (HIPIMS) as a new technology, which allows to obtain denser, smoother and better adhesive coatings with determined texture and morphology than other methods. The generally positive impact of reactive-element incorporation on the oxidation resistance of Al_2O_3 and Cr_2O_3 forming high temperature alloys is well known, e.g. [6]. At the present time there are no publications about the influence of yttrium on the oxidation behaviour of Cr_2AlC. In this work we have studied in detail the influence of the yttrium-content on the Cr_2AlC oxidation mechanism and its contribution to self-healing behaviour.

2. MATERIALS AND METHODS

For film preparation by HIPIMS a commercial system (CemeCon AG CC 800-9) and a compound Cr_2AlC target were used. Al_2O_3-plates were used as substrates. The substrate temperature was maintained at 400°C. These coatings were deposited without doping elements and with addition of Y in the range from 0.1 to 0.3 at.%Y. The coatings were isothermally annealed in the temperature range from 700 to 1200°C in flowing air up to 28h. Our films were characterised by SEM (Zeiss DSM 982 Gemini). Chemical composition analysis was performed by energy dispersive X-ray analysis (EDX) using acceleration voltage of 15kV. The structural analysis was carried out utilizing X-ray diffractometry (Bruker D8 Discover) using CuKα radiation with area detector VANTEC 2000. Grazing incidence diffraction (GID) method was employed to examine the structure of the thin films. From the characterization results a feedback for improving the synthesis conditions is expected.

3. RESULTS AND DISCUSSION

All deposited films are polycrystalline and consist only of Cr_2AlC. There exists a (110) texture, this means that the (110) and (001) planes are located parallel and perpendicular to the substrate surface, respectively, and the nanolaminates are growing perpendicular to the substrate surface and parallel to (001) plane (Figure 1). From the literature of the oxidation of Al-containing compounds it is known that at low temperatures metastable alumina phases are formed. At high temperatures there is a transformation into the stable α–form. We have found, that in contrast to this, Cr_2AlC forms stable α-Al_2O_3 at all temperatures in the initial phase of oxidation. Probably, oxygen is incorporated in the octahedral interstices of the upper Al-layer leading to formation of Al–O bonds which may act as nucleation sites for Al_2O_3 as described in [4] and shown in Figure 2 [4].

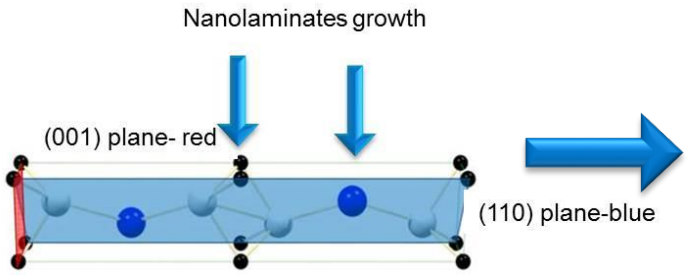

Figure 1: Unit cell of Cr_2AlC with marked position of the (110) and (001) planes.

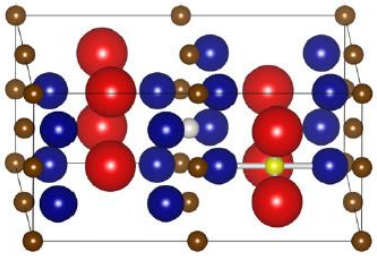

Figure 2: Super cell configurations considered for incorporation of oxygen in M_2AlC: M atoms-blue, Al-red, C-brown, O –yellow, carbon vacancy- white [4].

Preferred orientation (110) of the crystal growth in the MAX-phase thin films is a requirement for epitaxial growth of α-alumina crystals in the initial stage of oxidation at all temperatures.

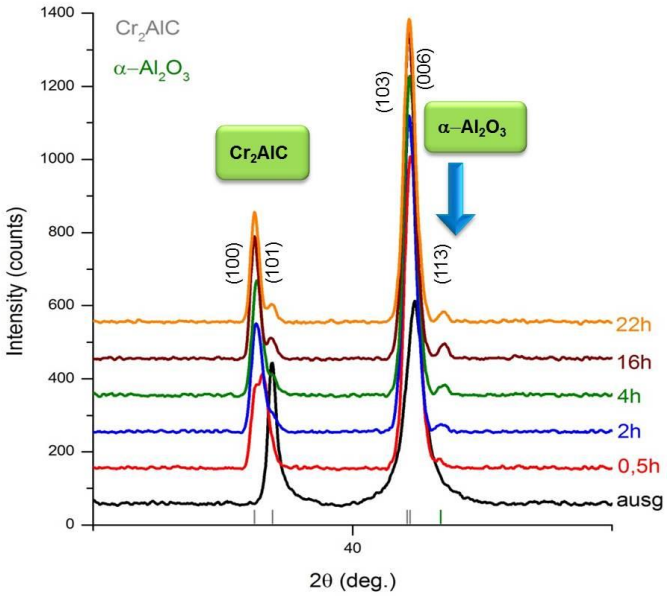

Figure 3: X-Ray diffraction pattern of the as-deposited coatings without Y and after annealing at 700°C for 0.5 - 22h.

We have found, that Y is located in the crystal lattice and does not segregate at the grain boundaries, as shown in [6] and slows down the bulk diffusion of Al-atoms. Oxide growth kinetics is mainly controlled by O anion inward transport. At high temperatures (800-900°C) the oxidation mechanism is changed. The formation and rapid growth of the metastable γ-Al_2O_3 from the α-Al_2O_3 scale for coating without Y was observed. Oxide growth kinetics is mainly controlled by Al cation outward transport caused by the concentration gradient of Al and O in α-alumina grains. As the result, the metastable γ-phase grows in the form of whiskers. The Y-atoms, which are probably located at the places of aluminium atoms at low solubility of Y in the MAX-phase, inhibit the necessary bulk diffusion of Al and Cr atoms and the formation of metastable γ-Al_2O_3 from α-Al_2O_3 scale during oxidation at high temperatures.
We have made Vickers indents with 200g load (Figure 4) in order to investigate the influence of 0.3at.%Y on oxidation induced crack-healing in the Cr_2AlC films at 900°C. After annealing at 900°C for 1h the cracks are completely healed by alumina.

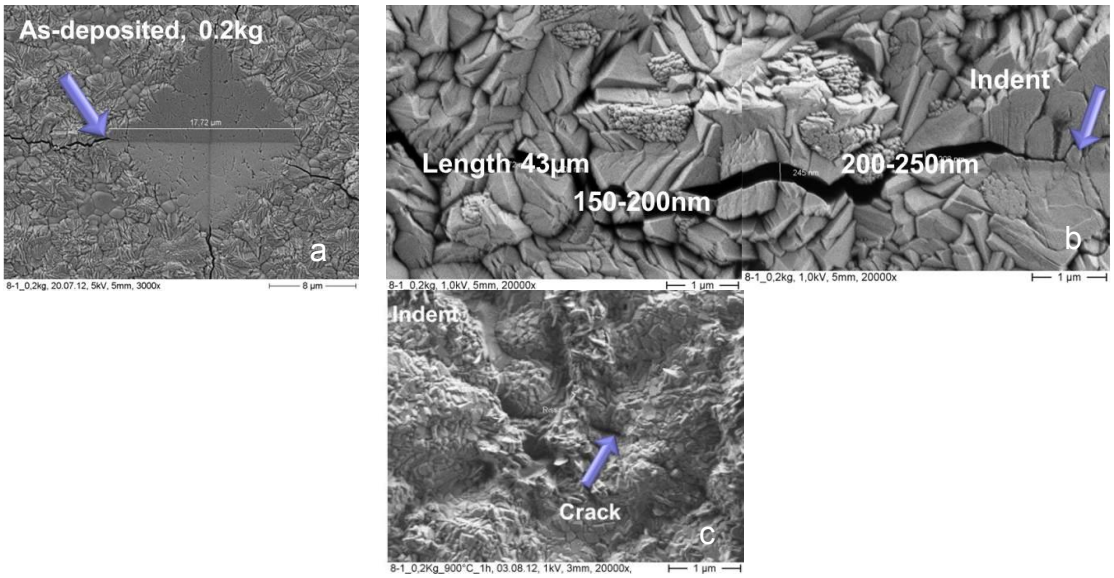

Figure 4: SEM images of the Vickers indents (a) and the crack propagation (b) at the surface of the as-deposited coating, (c) after annealing at 900°C, for 1h in air.

At 1200°C only α-Al_2O_3 is formed. The Al-concentration profile is presented in Figure 5a by the red line. There is an Al-rich area on the surface as a result of the α-alumina formation and an Al-depleted area underbeneath the surface. An enrichment of Cr occurs (blue line, Figure 5b) also directly beneath the α-alumina area as result of Cr_7C_3 formation. The concentration of Y is presented by the yellow line. Simultaneously, high Al-outward diffusion leads to $YAlO_3$ formation and an embrittlement of the film.

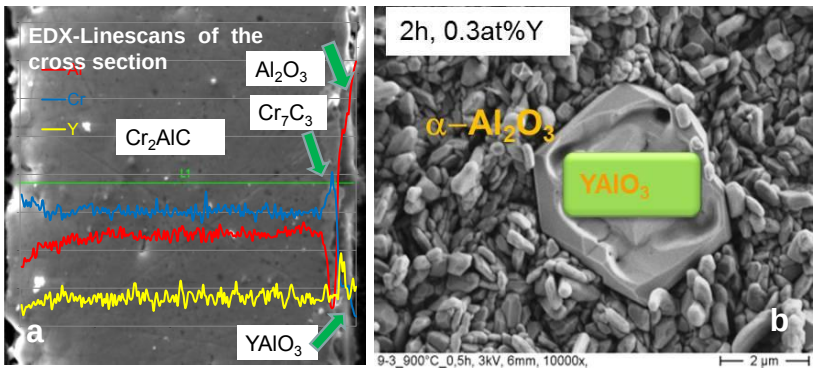

Figure 5: EDX-linescans of the cross section (a) and of the surface (b) of the Cr_2AlC-films with 0.3 at.%Y addition after oxidation at 1200°C for 2h.

Figure 6 shows the influence of 0.2 at.-% Y-addition on the crack healing during oxidation at 1200°C for 2 h.

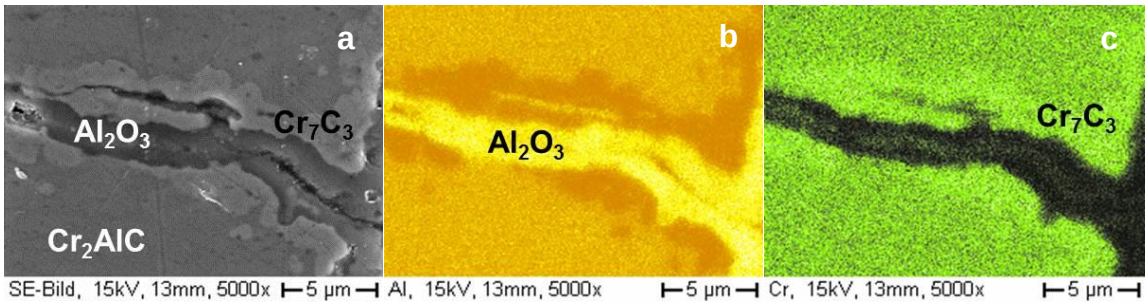

Figure 6: EDX-Mapping of the healed crack filled with alumina after annealing at 1200°C for 2 h of the Cr_2AlC coatings with 0.2 at.-% Y-addition.

4. CONCLUSIONS

In this work, we have determined the optimum Y-content for minimizing oxidation of the Cr_2AlC coatings. Simultaneously, with the same Y-content an optimum self-healing behaviour of cracks was found.

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