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Short communication

Filling of surface cracks in MAX phase ceramics using cathodic electrophoretic deposition

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Abstract

It is well known that surface defects, such as cracks, are electrochemical more active than a smooth surface and usually work like seeds for the deposition processes. The present work used this enhanced activity to locally deposit surface-charged Al_2O_3 and TiC micro and nano-particles into surface cracks in Ti_2AlC substrates. The formed deposit was compact and adhered well to the crack walls. A crack of about 30 μm could be filled with alumina particles in 10 min when applying 15 V and using a 5 wt% alumina suspension in ethanol. The deposition of TiC was more challenging due to coarseness of the particles. Grinding these particles to 1–2 μm yielded a very stable suspension and an improvement in the crack filling behaviour.

Keywords: MAX phase ceramics; Electrophoretic deposition

1. Introduction

MAX phases ceramics are ternary compounds with the general formula $M_{n+1}AX_n$ (where M is an early transition metal, A is an A-group (mostly IIIA and IVA) element, X is C and/or N, and n range between 1 and 3 [1]. They have gained worldwide interest due to their unique combination of metallic and ceramics-like properties [2]. Like metals, MAX phases ceramics have a high thermal and electrical conduction, good machinability, and are resistant to thermal shock; They have high melting points and high thermal stabilities similar to those of ceramics [3,4]. However, as applies to all materials, MAX phases ceramics can incur various type of damage caused by the environment or the operating conditions ultimately leading to sample failure. This failure starts usually by surface cracks that propagate dynamically into the interior parts of the material. Here we introduce a method to fill the crack with ceramic powder at room temperature [5]. Upon subjecting the filled crack to its (high) operating temperature, mutual diffusion can take place between the filler and the MAX substrate causing the crack to close completely [5,6].

We have selected Ti_2AlC as the most suitable MAX phase material because of the large number of publications on the properties of this material and its reported attractive crack closing reactions upon exposure to oxygen containing atmospheres at high temperatures [7–13]. We have chosen alumina and titanium carbide as the fillers based on their reported ability to adhere well to the MAX phase material [12,14,15]. In addition, the availability of these materials in the powder form with different morphology and particles size allowed us to study different factors that might affect the crack filling process.

In order to introduce a crack in Ti_2AlC ceramics in a controllable manner, a Vickers indentation (load of 200 N) was introduced on the sample surface. This caused cracks of the size 20 to 60 μ at the tip of the indentation. The depth of the crack was investigated using confocal microscopy. Fig. 3(a) indicated that the crack has a triangular prism shape with the depth range between 60 and 120 μ.

The alumina or titanium carbides were deposited using a controlled electrophoretic deposition technique that allowed depositing the filler particles locally in the cracked zone. To avoid corroding the substrate material, cathodic

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electrophoretic deposition (EPD) was used. Prior to deposition the Al_2O_3 and TiC particles were suspended in ethanol and the positive charge was introduced by the keto–enol equilibrium reaction catalysed by Iodine and H_2O, and the succeeding reaction between enol-acetone and iodine giving H^+ on the surface of the suspended alumina particles according to reaction (1) and (2) [16]. The EPD was carried out in a two-terminal cell with the cracked Ti_2AlC sample serving as the cathode and 2 mm Al rod as an anode. The initial average particle sizes for Al_2O_3 and TiC were 1 and 3 μm, respectively. When applying a potential difference of 20 V for 5 min, a first deposit of alumina powder was observed at the bottom part of the crack (Fig. 1). By increasing the EPD time, more alumina deposited in the crack. At around 15 min the whole crack was filled by alumina particles (Fig. 2a). Applying larger potential differences or depositing for longer times resulted in additional deposition of the powder in the area around the crack (Fig. 2b). The confocal images of the sample after different period (Fig. 3) confirmed these results and indicate that the alumina deposition was homogeneous across the cross section of the crack.

$$CH_2COCH_3 \overset{H_2O,\ I_2}{\leftrightarrow} CH_3(OH)CH_2 \quad (1)$$

$$CH_3C(OH)CH_2 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^- \quad (2)$$

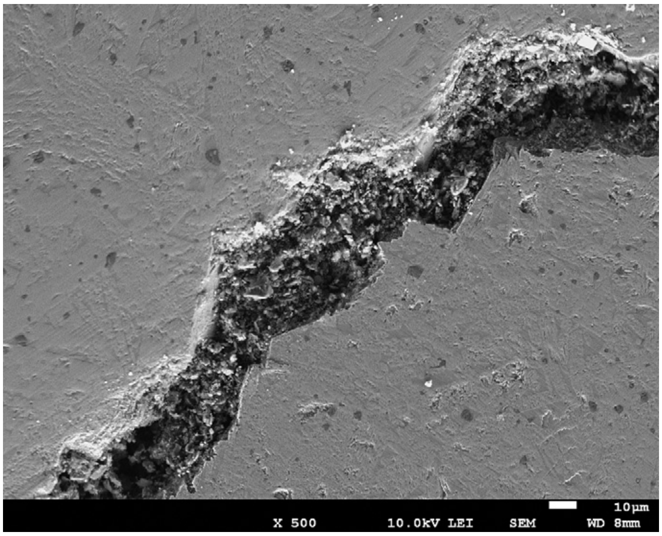

Fig. 1. SEM image for the surface crack after cathodically polarized the Ti_2AlC sample for 5 min at 20 V in 10 wt% alumina suspension.

To study the effect of the particles size on the crack filling process, the as-received alumina was subjected to ball milling for different periods of time using tungsten carbide balls. As expected, the packing density of the filling materials in the crack increased when decreasing the average particle size. However, for nanometer-sized particles, the ceramic filling formed internal cracks upon drying at 200 °C (Fig. 4).

While the majority of the alumina particles deposited on the MAX phase sample on the cathode, some alumina particles were detected on the aluminium anode. That is because when the particles in the suspension are treated with ethyleneglycol it tends to adsorb some I^- ions rather than protons, which results in the existence of some negatively charged particles [17]. The ratio of the negatively charged particles seems to increase by decreasing the particles size, as more anodic deposition was observed when nano particles of alumina was used as the feed materials. Therefore, another dispersant was tested. During the preparation of the initial suspension, 0.4 ml of acetylacetone was sonicated with Al_2O_3 in ethanol for 24 h before adding the charging solution (iodine in water and acetone). After applying 20 V difference between Ti_2AlC sample and Al rod, a very dense filling was obtained in the crack after only 5 min of polarization (Fig. 5).

Dense fillings were also formed in the crack when reducing the concentration of the alumina particles in the suspensions from 10 to 5 wt%. However, reducing the concentration of the alumina further to 1 wt% led to a strong increase in the time required to deposit material in the crack. It was only after 30 min of applying 20 V when some deposit was attached to the cracked zone in the MAX sample.

It is a matter of logic that the functionality of the treated samples will be closer to that of the un-cracked sample if the crack is filled with powders that have properties similar

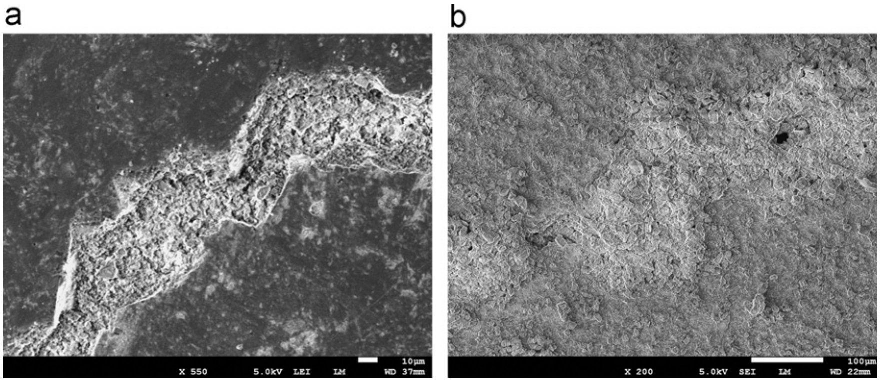

Fig. 2. SEM images for the surface crack after cathodically polarized the Ti_2AlC sample for (a) 15 min and (b) 20 min at 20 V in 10 wt% alumina suspension in ethanol.

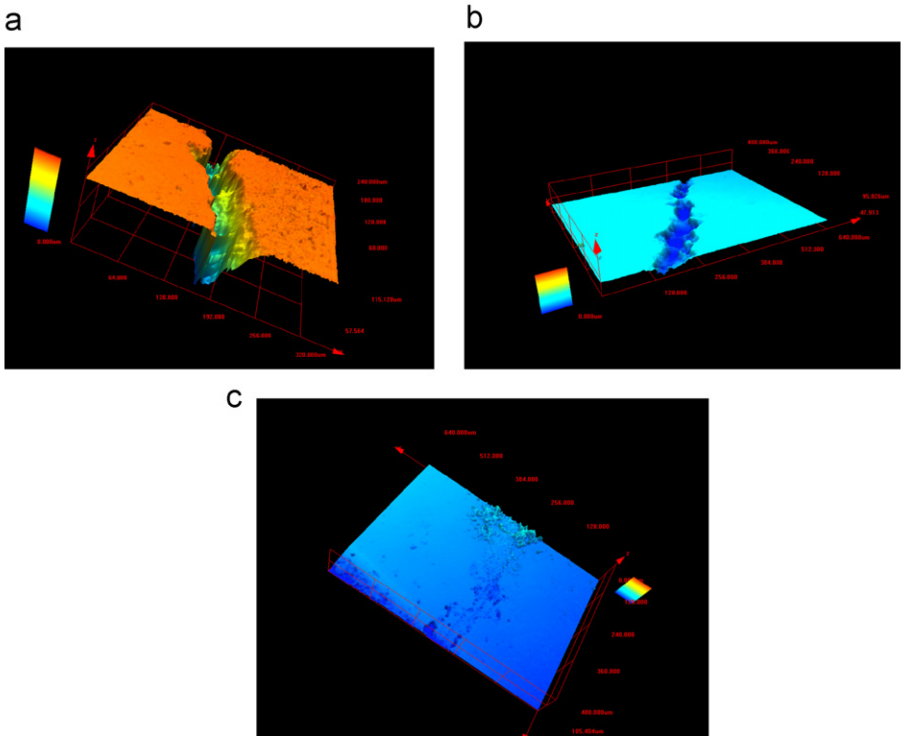

Fig. 3. The confocal images for (a) the crack introduced on the surface of the Ti_2AlC sample, (b) and (c) are after cathodically polarized the Ti_2AlC sample at 20 V in 10 wt% alumina suspension for 5 and 15 min, respectively.

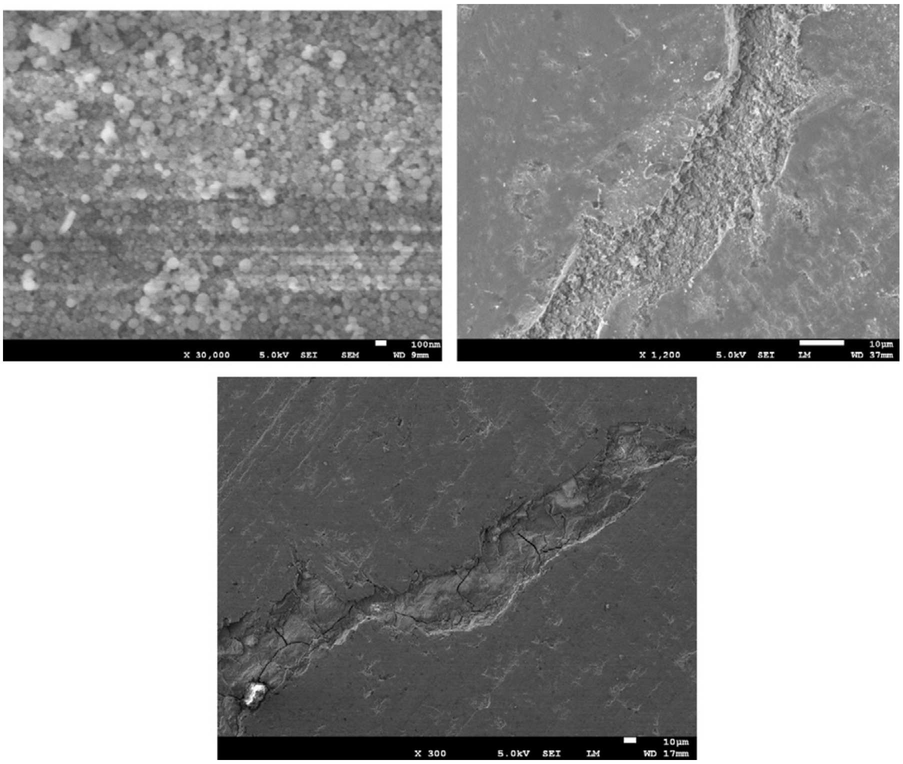

Fig. 4. Effect of the particles size on the alumina deposition.

to those of the substrate material. For that reason, we have selected titanium carbide as the filling material for cracked Ti_2AlC sample. TiC powder was treated with acetylacetone and suspended in ethanol. Fig. 6 shows the Ti_2AlC sample after applying 20 V potential difference for 30 min. Although there were TiC particles deposited into the crack, the packing

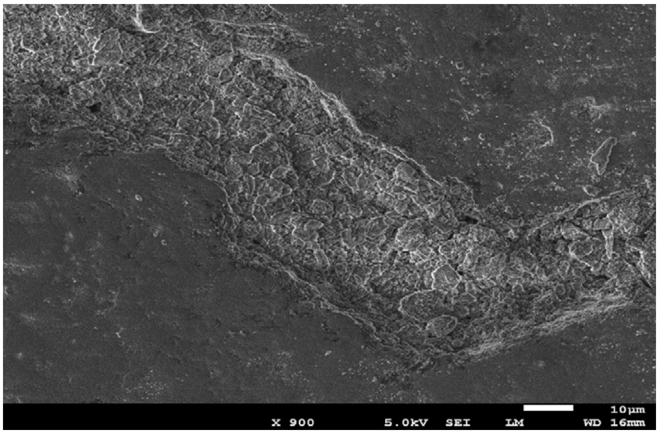

Fig. 5. Dense filling obtain in the crack after cathodic EPD of alumina from ethanol suspension treated with acetylacetone.

of these particles is very poor and there was almost no adhesion between the filler and the surface of the Ti_2AlC sample. The coarse particle size reduced the mobility of the TiC powder in the suspension. In addition, the smooth faceted-surface of the particles led to poor charging in the suspension and a significant decrease of the effect of the applied electric current.

As shown for alumina particles, reducing the average particle size proved to produce more compacted deposits in the crack. However, grinding the TiC particles is a non-trivial process. 24 h of ball milling was required to reduce the average particle size to 1–2 µm. The morphology of the particles after grinding also changed as the fine particles have rough edges instead of the smooth surfaces (Fig. 7). After EPD at 20 V for 30 min, a one-particle-thick layer is formed on the area around the crack. The deposit in the

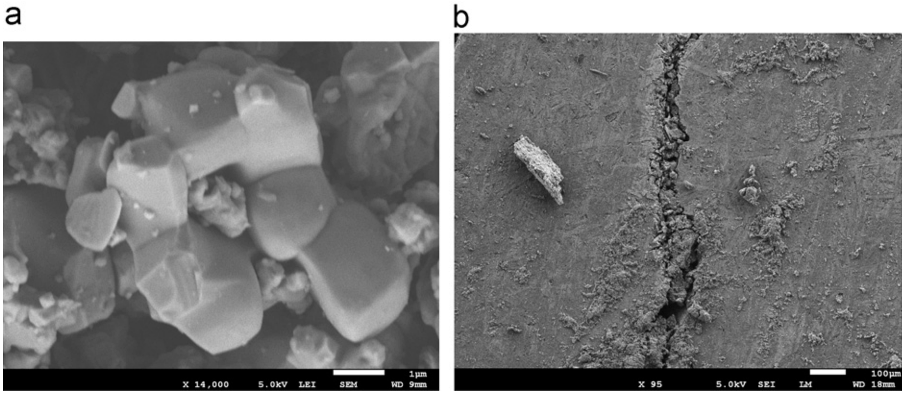

Fig. 6. SEM images for (a) the as received TiC powder, and (b) the cathodic EPD of it in a surface crack on Ti_2AlC sample.

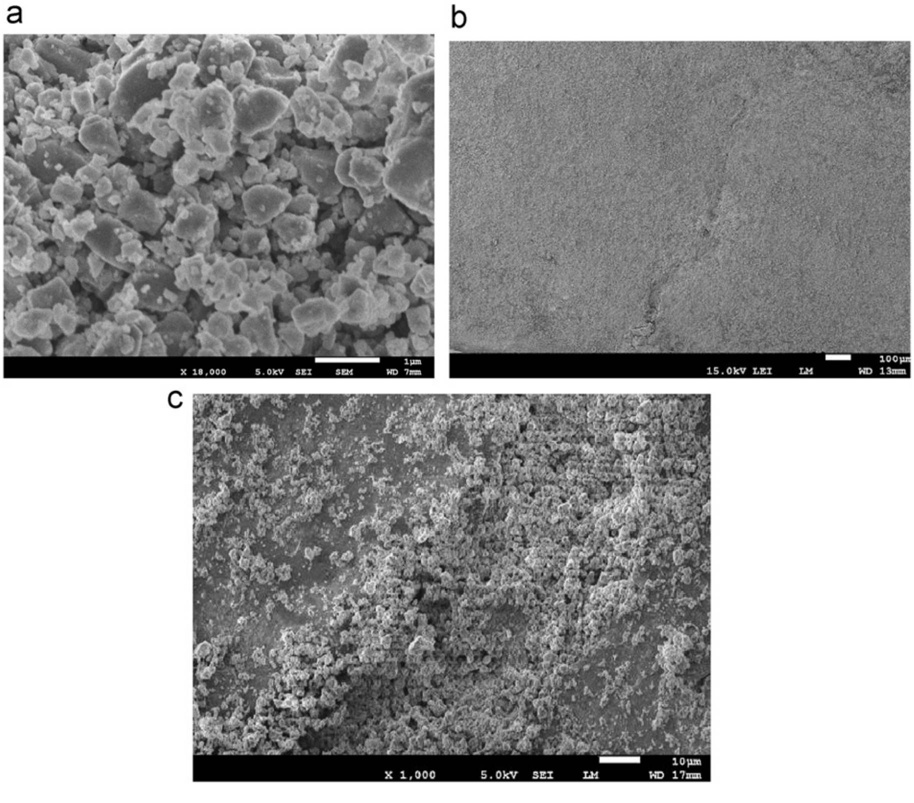

Fig. 7. (a) SEM Images for the TiC powder after ball milling for 24 h (b) and (c) are different magnifications of the deposited particles on Ti_2AlC sample.

crack is denser then that obtained by EPD with the as received carbide. It is to be expected that a more compacted deposit could be achieved if the particles size reduced further using a very long ball-milling step.

Summarizing, in this paper it is shown that it is possible to control the deposition of surface-charged particles on the imperfection zones, i.e., cracks, of conductive surfaces. These particles tend to form well-adhere dense filling inside the crack, which, if subjected to a proper medium temperature heat treatment, will restore the materials functionality. This proof-of-concept work is promising as it introduces an affordable technique to recycle damaged materials without the need of extensive heating or consuming the substrate materials as in the case of oxidative healing. The new process is tuneable and in principle even allows filling the cracked zone with materials that could improve the original performance of the substrate material.

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