The response of Ti$_3$SiC$_2$, Ti$_3$AlC$_2$, Ti$_2$AlC and Cr$_2$AlC MAX phases under simulated primary water has been explored for the first time. Samples were tested for 28 days in 300 °C water with the addition of 2 ppm LiOH. The Ti-based MAX phases formed oxides of TiO and TiFeO$_3$. X-ray diffraction and scanning electron microscopy showed no evidence of a passive Al or Si-based layer forming during testing. A-layer dissolution was observed to cause delamination of the layered structure. In contrast, Cr$_2$AlC showed little change during autoclave testing, suggesting that a thin passivating chromia layer was formed.

1. Introduction

The MAX phases are potential materials for nuclear applications due to their unique mix of ceramic and metallic properties. The MAX phases are so called as M is an early transition metal, A is an A-group element and X is either carbon or nitrogen. They have a nano-layered hexagonal crystal structure comprising of MX layers separated between single atomic layers of A. In general, they have relatively low hardness for an inherently ceramic material (1–5 GPa [1]) but they are still harder than most metals. Some limited tribology work on the basal plane of a single crystal also suggests exceptionally low coefficients of friction, μ, of 2–5 × 10$^{-3}$ [2].

MAX phases are a proposed material for use in nuclear reactors as accident tolerant fuel coatings (ATFCs) [3] and for wear resistance applications [4]. Although ATFCs must show good resistance to loss of coolant accidents (LOCA), first and foremost they must function and show minimal oxidation during normal operating conditions. Current Zr-based cladding materials suffer from excessive oxidation and subsequent hydrogen production during LOCA [5]. Therefore, oxidation of cladding during LOCA should be minimised to increase coping times. MAX phase coatings of Ti$_2$AlC have shown to be beneficial in impeding oxidation of Zircaloy-4 in steam up to 1005 °C [3].

Aluminium containing MAX phases, such as Ti$_3$AlC$_2$ and Ti$_3$AlC, have been observed to form dual-layered oxides during high temperature (> 900 °C) air testing [6,7]. The oxide formed comprised an inner layer of α-Al$_2$O$_3$ and an outer layer TiO$_2$ (rutile). Ti$_3$SiC$_2$ also forms a dual oxide with a rutile outer layer, with the inner layer being a mixture of SiO$_2$ and rutile [8]. Cr$_2$AlC was shown to only form an Al$_2$O$_3$ layer with an Al depleted layer beneath [9]. Voids were also observed to have developed in the Al depleted regions.

There is little literature which investigates the response of MAX phases to normal operating conditions, i.e. high temperature and pressure water. The oxidation of Ti$_3$AlC$_2$ and Ti$_2$AlC in supercritical water of 500 °C at 25 MPa with a concentration of 20 ppb oxygen for 100 h was studied by Du et al. [10]. It was shown that the corrosion resistance in these compositions was superior when the exposed sample surface had a strong basal texture (i.e. A-layers are parallel to the surface). In this case, a protective Al$_2$O$_3$ layer was formed. It was postulated that when the basal planes are perpendicular to the surface, the A-layers are exposed, thus resulting in easier Al removal or oxidation. The strongly basal textured samples showed higher oxidation and also cracks which align with the basal plane.

Corrosion studies on other coatings for Zr cladding have been performed by Alat et al. in a static autoclave in pure water at 360 °C and 18.7 MPa on TiAlN with a Zr-Nb-Sn-Fe alloy (ZIRLO) substrate to compare oxidation rates [11]. The results from their work showed undesirable formation of boehmite (γ-AlO(OH)) during testing, which could be inhibited with the addition of a TiN coating on top of the
existing TiAIN. A more recent study by Alat et al. investigated this further by producing multi-layered TiN-TiAIN coatings, which showed no Al migration, thus avoiding boehmite phase formation [12].

Ti3AlC2, Ti3AlC, Ti3SiC2, and Cr2AlC show good performance during high temperature air and steam testing, it is not known if these materials will show equally good responses during prolonged durations in LWR coolant water conditions. Autoclave experiments with correct water chemistry is required to understand the response of MAX phase materials during normal operating conditions in light water reactors (LWRs). For the first time, simulated primary water autoclave testing is performed to determine their suitability during normal reactor operation. Furthermore, for the application of a more costly cladding to be economically viable, it is important that it provides benefit during normal operation and not just in an accident scenario.

2. Experimental methods

2.1. Materials

Samples of Ti3SiC2, Ti3AlC2, Ti3AlC and Cr2AlC were acquired from Drexel University with details of their manufacture available from [13,14]. All Ti-based MAX phases were ∼95 wt.% pure with the remaining material being TiC. Samples were electrical discharge machined (EDM) into 10 × 10 × 2 mm3 coupons, which were subsequently ground and polished to a mirror finish. Samples were cleaned with soap and rinsed with ethanol prior to autoclave testing.

2.2. Autoclave testing

Autoclave tests were performed at the Manufacturing Technology Research Laboratory (MTRL) at the University of Manchester. Flowing autoclave testing was performed at 300 °C, 12 MPa, <5 ppb O2, 3 ppm H2, 2 ppm Li (as LiOH) and samples were tested for 28 days. The addition of LiOH, which has a molarity of 8.3507 × 10−3, results in a water pH of 7.5 at 300 °C. Samples were suspended through pre-drilled Ti3SiC2 using a Bruker D8 Discover with a Co (H2O were assumed. It should be noted that the results do not take into account pH changes or changes in oxygen partial pressure, and therefore only provide qualitative information about potential corrosion products.

Pourbaix diagrams used to determine equilibrium phases in the autoclave environment were calculated using HSC 6.0 Outotec software, where molarities of 1 × 10−6 for each element (Al, Si, Ti and Cr) in H2O were assumed. It should be noted that the results do not take into account pH changes or changes in oxygen partial pressure, and therefore only provide qualitative information about potential corrosion products.

2.3. X-ray diffraction

X-ray diffraction (XRD) was performed on Ti3AlC2, Ti3AlC and Ti3SiC2 using a Bruker D8 Discover with a Cu (λ = 1.54 Å) Göbel mirror to give a parallel beam for grazing incidence (GI) scans. Scans were performed with incidence angle of 9° using a 0.1 mm slit in the vertical and a 5 mm slit in the horizontal direction. The scanned two-theta range was 25° to 80° with a step size of 0.02° and counting for 4 s per step. A 2.5° Soller slit was used before the detector to increase peak resolution. The Ti-based MAX phases were scanned using a Co X-ray source to avoid fluorescence from the Fe present in the samples post-testing. The Cr2AlC was scanned on the Bruker D8 Advance using a Cu (λ = 1.54 Å) Göbel mirror for GI scans. The penetration depth of X-rays for each sample is estimated to be 3.3 μm, 3.4 μm, 3.5 μm and 4.0 μm for Ti3SiC2, Ti3AlC2, Ti2AlC and Cr2AlC, respectively.

2.4. Microscopy

Scanning electron microscopy (SEM) was carried out on a Quanta 650 FEG-SEM using 20 keV accelerating voltage, spot size 4.5 and a working distance of 10 mm. Energy dispersive spectroscopy (EDS) point scans were performed for 60 s and analysed using Oxford Instruments Aztec software. Electron transparent samples were extracted using the FEI Quanta 3D focused ion beam (FIB). A 1.5 μm Pt layer was deposited first to protect the surface features and an initial lamella of 10 × 5 × 1 μm3 was cut from the bulk sample using a 7 nA beam current. Thinning stages were performed using successively lower currents. A final cleaning stage using 2 keV and 16 pA was performed to reduce ion implantation. Scanning transmission electron microscopy (STEM) was performed on a FEI Titan G2 80-200 TEM/STEM with ChemiSTEM Technology operating at 200 keV with probe current of 1.6 nA and a convergence angle of 21 m rad. High spatial resolution is achieved with a spherical aberration (Cs) corrector. The ChemSTEM® system comprises four X-ray EDS detectors to acquire high-resolution elemental maps and linescans. Electron energy loss spectroscopy (EELS) was performed on a Cs− aberration corrected Nion UltraSTEM with a Cold-FEG. Operations were performed at 100 kV accelerating voltage with a convergence angle of 31 m rad. EELS spectra were collected on a Gatan Enfinia spectrometer with 0.3 eV ch⁻1, in the energy loss range of 390 to 1004 eV.

3. Results

3.1. Surface analysis

Surface images of Ti3SiC2, Ti3AlC2 and Cr2AlC before autoclave testing are shown in Fig. 1A–C, respectively. Low magnification micrographs of Ti3SiC2 and Ti3AlC2 after autoclave testing are shown in Fig. 1D and E, respectively. The before and after autoclave images are not taken from the same region of the sample. After testing, it is observed that large faceted growths (indicated by a red arrow in Fig. 1D) have formed and the surface is uneven, no longer appearing polished. The Cr2AlC sample shows no observable change from pre-autoclave (Fig. 1F) and has retained a polished surface. There are some pores in Cr2AlC (indicated by a red arrow in Fig. 1C and 1F), which are already present before exposure and appear not to have a deleterious impact on the corrosion response. Higher magnification images of Ti3AlC2 and Ti3SiC2 away from any large growths (Fig. 1G and H respectively) highlight the uneven surface between the larger growths that is comprised of smaller, sub-micron features. Observation of the higher magnification Cr2AlC image (Fig. 1I) after autoclave testing again show no growths or corrosion features on the surface.

The same faceted growths are observed on all Ti-based MAX phases tested; growths on the Ti3AlC sample are shown alongside elemental maps of the same region in Fig. 2. The elemental maps show that these growth features are Ti and Fe-rich oxides. Qualitative compositions of the features and of the materials surface are obtained by averaging over 5 EDS point scans, where each scan was performed on a different growth product; the results of this are tabulated in Table 1. Small amounts of Mn were also detected by EDS, which is also believed to originate from the steel autoclave. The values stated after averaging are all under 1% standard error. The composition of Cr2AlC is very similar before and after testing with only a small increase in oxygen content. This would suggest a thin protective Cr2O3 has formed during corrosion testing which inhibits further oxidation or elemental leaching. All Ti-based MAX phase samples show an increase in oxygen, at the expense of MAX phase elements, near to the surface. The growth features seen on all surfaces appear to be roughly the same composition of ilmenite, FeTiO3.

3.2. X-ray diffraction analysis

Pristine and autoclave tested samples were analysed by XRD to determine phase changes during testing. Diffraction patterns of the four MAX phase samples are shown in Fig. 3. The diffraction pattern of Cr2AlC remained unchanged after autoclave testing. All Ti-based MAX
Fig. 1. Secondary micrographs of the surfaces of Ti$_3$SiC$_2$ (A), Ti$_3$AlC$_2$ (B) and G$_2$AlC (C) before autoclave testing. Secondary electron micrographs of Ti$_3$SiC$_2$ (D and G), Ti$_3$AlC$_2$ (E and H) and Cr$_2$AlC (F and I) after autoclave testing at 300 °C for 28 d. The top images are at 1,000× magnification and the bottom images are at 10,500× magnification, the red-boxed region in the low magnification images indicate the location of the high magnification images. The red arrow in (D) indicates growths out of the surface and the red arrow in (C and F) indicates pores inherent in the Cr$_2$AlC sample (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Fig. 2. SE SEM micrograph of Ti$_2$AlC after autoclave testing at 300 °C for 28 d. The elemental maps of the same area as the SE image for Ti, O, Fe and Al are shown also.
phase samples showed the same formation of FeTiO$_3$ and TiO. The TiO reflections have been identified as having a rhombohedral unit cell with lattice parameters of 4.08 Å and 14.1 Å for a and c, respectively. There are no reflections in any diffraction patterns which match with an aluminium oxide or silicon oxide.

### 3.3. Cross section analysis

To gain a better understanding of the corrosion mechanism that lead to the observed features, cross-sections of Ti$_3$AlC$_2$ and Ti$_3$SiC$_2$ were examined in the TEM. The cross-section of Ti$_3$AlC$_2$ is shown in Fig. 4, where a depletion of Al at the surface is observed along with an O and TiO enrichment. This correlates with XRD results showing only the presence of the MAX phase, TiC, TiO and TiFeO$_3$. No areas of Al and O enrichment overlap, suggesting no protective alumina layer has formed, which again correlates with the XRD data.

Fig. 5 shows a high-angle annular dark-field (HAADF) TEM micrograph of the Ti$_3$SiC$_2$ cross section where the TiFeO$_3$ growths on the surface are again clearly visible. The underlying material appears striated under the TiFeO$_3$, which is believed to correlate with the layered structure of the MAX phase. The elemental maps of the red boxed region in the HAADF image show O ingress down the grain boundary, as well as following the striations. The Fe map shows there is also a concentration of Fe down the striations, but to a lesser extent than O. Si has been depleted from the grain boundary, and in the neighbouring region, whilst this region is both O and Ti rich suggesting the formation

| Table 1 | Qualitative elemental compositions of the four pristine MAX phase samples and after testing. The Surface values are for regions of material with no growths and the outward growth values are for the growth features seen in the micrographs in Figs. 1 and 2. The values stated are average values over 5 separate EDS points scans on different areas of the same type of feature. |
|----------------|----------------|----------------|----------------|----------------|
| Element        | Ti$_3$SiC$_2$  | Ti$_3$AlC$_2$  | Ti$_2$AlC      | Cr$_2$AlC      |
|                | Pristine | Surface | Growth          | Pristine | Surface | Growth          | Pristine | Surface | Growth          |
| Ti (wt. %)     | 72      | 61     | 31              | 72      | 57     | 31              | 70      | 50     | 29              |
| Cr (wt. %)     | –       | –      | –               | –       | –      | –               | –       | –      | –               |
| Al (wt. %)     | –       | –      | –               | –       | –      | –               | –       | –      | –               |
| Si (wt. %)     | 13      | 5      | –               | 14      | 8      | –               | 13      | 6      | –               |
| C (wt. %)      | 15      | 11     | 4               | 14      | 7      | 5               | 17      | 27     | 6               |
| Fe (wt. %)     | –       | –      | 32              | –       | –      | 31              | –       | –      | 29              |
| Mn (wt. %)     | –       | –      | –               | –       | –      | –               | –       | –      | –               |
| O (wt. %)      | –       | 23     | 31              | –       | 28     | 31              | –       | 17     | 34              |
|                | –       | –      | –               | –       | –      | –               | –       | –      | –               |

**Fig. 3.** X-ray diffraction patterns of Ti$_3$SiC$_2$ (A), Ti$_3$AlC$_2$ (B), Ti$_2$AlC (C) and Cr$_2$AlC (D) before (top pattern) and after (bottom pattern) autoclave testing collected at an incidence of 9°. The red lines indicate ilmenite (FeTiO$_3$); the green lines indicate TiO. All other peaks are associated with the MAX phase or pre-existing binary carbides (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
of TiO.

A higher magnification micrograph of the yellow-boxed region in Fig. 5 is shown in Fig. 6, along with EDS maps of the red boxed region. It appears that the striations observed are delaminations in the MAX phases layered structure. The elemental maps of these delaminations show correlation between O-rich regions and those depleted in Si. Streaks of Fe enrichment are also observed which implies that Fe diffuses down the delaminated regions. A nano-void is highlighted in the HAADF and elemental maps in Fig. 6 by the orange oval.

A similar cross-sectional region such as in Fig. 6 was examined using EELS to further identify the phases with in the oxide structure. A HAADF image of the region along with EELS spectra indicating the different phases are shown in Fig. 7. The EELS spectra confirm the presence of TiO as there is a peak shift in the Ti L edge from Ti$_3$SiC$_2$ to TiO to higher energy losses, which suggests an increase in oxidation state.

A higher magnification image of the yellow-boxed region in Fig. 7 is shown in Fig. 8. This region is away from TiFeO$_3$ phase, which has grown down the layered structure of the MAX phase. It is observed that O has penetrated further down the layers than Fe. This is indicative that the TiO is formed ahead of TiFeO$_3$. Furthermore, the O and Fe appear to transport down the layers via the faces of the delaminated layers. The orientation of the original Ti$_3$SiC$_2$ grain is shown in the HAADF image of Fig. 8, whereby the basal planes are aligned parallel to the advancing Fe and O paths. There is no Si present in the delaminated area, ahead of the O and Fe ingress, therefore the faces of the delaminated layers are equivalent to the (111) TiC planes. There is no evidence in the region examined that Fe or O permeate through the close packed layers (i.e. along the c-axis), only along the a/b-axis.

The cross section of Cr$_2$AlC shown in Fig. 9A shows the entire FIBed sample after autoclave testing. No significant changes to the microstructure were observed. A higher magnified image of the yellow-boxed region in Fig. 9A is shown in Fig. 9B. Fig. 9C shows the presence nano-voids approximately 2–3 nm to the surface, within region II. The EDS line scan in Fig. 9D is of the region marked from 1 to 2 in Fig. 9B, thus from sample surface into the bulk. The line scan shows 3 distinct regions with regards to the elemental composition. Region I is a Cr and Fe rich oxide at the surface of the sample. Region II is a Cr depleted region which could be a mixture of Al$_2$O$_3$ and chromia, Cr$_2$O$_3$. Region III is the unaffected Cr$_2$AlC material which starts between 5 and 10 nm from the surface.

3.4. Corrosion products

To better understand the corrosion processes, the thermodynamically stable corrosion products have been calculated. The pH of the simulated primary water at 300 °C with the addition of 2 ppm LiOH is calculated to be pH 7.5. The thermodynamically stable corrosion
products of Cr, Ti, Al and Si in 300 °C water are shown in the Pourbaix diagrams in Fig. 10. The Cr Pourbaix diagram (Fig. 10A) shows that Cr₂O₃ is the stable corrosion product during testing, which match the STEM analysis in Fig. 9. The Ti system (Fig. 10B) would suggest that TiO₂ is stable, however the reduced oxygen content would lead to the stable TiO phase being present instead. The Si system (Fig. 10C) shows that SiO₂ is not stable in the pH range of testing, but will form aqueous silicate acid (HSiO₃). In the Al system (Fig. 10D) it is observed that aluminium hydroxide (Al(OH)₄) is the stable corrosion product in the testing pH range. It should be noted that the comparison between Pourbaix diagrams and experimentally observed phases are qualitative, as partial pressure of O₂ and H₂ in the system are not considered.

4. Discussion

4.1. Ti-based MAX phase response to simulated primary water

All Ti-based MAX phases studied formed the same phases - TiO and TiFeO₃ - as a result of autoclave testing as demonstrated by the XRD patterns (Fig. 3A–C). This implies that a similar corrosion mechanism occurs in each material. The presence of alumina or silica was not observed after testing through EDS, EELS or XRD analysis. This is in contrast with the work by Zhang et al., who performed autoclave testing on Ti₃AlC₂ and Ti₃SiC₂ at 500 °C–700 °C under 35 MPa in a gold coated autoclave in pure water [15,16]. In both cases, Zhang et al. report the formation of anatase and/or rutile, depending on test temperature. In the current autoclave work the formation of TiO is observed. The EELS investigation has shown the reduction of Ti valence in the Ti₃SiC₂ structure to Ti²⁺ in TiO and then TiFeO₃ (Fig. 7). The low O₂ concentration during testing (< 5 ppb) could explain the formation of TiO rather than TiO₂. Ilmenite formation can also accommodate small amounts of Mn in the Fe positions, which may explain the small amount of detected Mn by EDS (Table 1). The presence of Fe and Mn in the water is not believed to accelerate corrosion as Ilmenite is not observed to be prevalent, but is only observed in the larger surface growths.

4.1.1. Corrosion mechanism

As illustrated in Fig. 10, neither SiO₂ nor Al₂O₃ are thermodynamically stable at the pH found in primary water. Therefore, all
MAX phases relying on these oxides for passivation are unlikely to perform well in similar aqueous environments. The removal of Al/Si from the MAX phase is postulated to proceed as:

\[
\text{Ti}_3\text{SiC}_2(s) + 3\text{H}_2\text{O}(l) \rightarrow \text{Ti}_3\text{C}_2(s) + \text{H}_2\text{SiO}_3(aq) + \frac{3}{2}\text{H}_2(g)
\]

\[
\text{Ti}_3\text{AlC}_2(s) + 3\text{H}_2\text{O}(l) \rightarrow \text{Ti}_3\text{C}_2(s) + \text{Al(OH)}_3(aq) + \frac{3}{2}\text{H}_2(g)
\]

The remaining TiC layers are exposed to water and O2 and oxidise by:

Fig. 8. HAADF STEM image of the yellow-boxed region in Fig. 7 with element maps of the red-boxed section acquired by EELS. The Ti, O and Fe maps were acquired from EELS spectrum values in the range of 455–468 eV, 706–711 eV, and 530–536 eV, respectively (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Fig. 9. HAADF STEM micrograph of Cr2AlC after autoclave testing of the whole sample (A), high magnification image of the yellow box in A (B) and a high magnification image of the yellow boxed region in B (C). The EDS linescan in (D) is of the red lined region between 1 and 2 in B. The three sections within the line scan show I) Cr and Fe rich oxide, II) Cr depletion region and III) is Cr2AlC (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
The 4 different stages identified for the proposed mechanism for corrosion are highlighted in Fig. 11. In the first stage the pristine MAX phase is subjected to the environment. The second stage sees the Si/Al layers being removed when there is an ingress of oxygen. The Al vacancy formation (VA) has been shown to be promoted by the incorporation of oxygen, which weakens the neighbouring Ti-Al bonds in Ti$_2$AlC [17]. This is a detrimental effect as it increases the diffusion of oxygen along the Al layers leading to more rapid delamination. The third stage is the oxidation of the remaining TiC layers, which results in the delaminated regions being TiO rich. It is believed that both inward diffusion of O will continue down the A-layers, thus resulting in further formation of TiO striations. The phase transformation is from cubic TiC...
phase with, from XRD analysis, an a-lattice parameter of 4.33 Å to the tetragonal TiO phase with an a-lattice parameter and c-lattice parameter of 3.78 Å and 9.42 Å, respectively. The associated volume expansion associated with this transformation may explain the observed increased delamination. The fourth stage is the continuation of Ti oxidation out of the layers to form small TiO microcrystals at the surface. The Fe present in the water also reacts with the TiO, resulting in the formation of TiFeO₃.

4.2. MAX phases in a nuclear environment

The application of MAX phases in a nuclear environment has focused recently on their use for ATFCs. Neutronics analysis has suggested that coating thickness, for Ti₃AlC₂, should not exceed 25 μm when used in a light water reactor environment [18], a coating thickness also supported by other research into the neutronics penalty from coating additions [19]. The oxygen ingress down the Ti₃SiC₂ grain boundary, as presented in Fig. 5, is approximately 1.5 μm into the sample within only 28 d. It is worth pointing out that the autoclave test-temperature was 300 °C, i.e. similar to operating temperatures of light water reactors. As the material does not develop a passivating oxide layer, it is fair to assume that such oxygen ingress will continue at a similar rate reaching the substrate in a few hundreds of days.

Further investigation is required to assess the effects of tensile stress applied during corrosion testing, as it is believed this would deteriorate the coating performance. Such stresses could be a result of thermal expansion mismatches with the substrate, irradiation induced growth and creep or fuel swelling during operation. The striations seen in the HAADF image in Fig. 5 correlated with the A-layers of the MAX phase hexagonal structure. Further analysis showed that there was a preferential attack on the A-layers, suggesting that certain grain orientations, which expose the A-layers, are more likely to corrode. These specific grain orientations and grain boundaries are more susceptible to intergranular oxidation and will act as stress concentration sites resulting in crack propagation through the coating. Cracking of MAX phases has been observed in Ti₃AlC₂ and Ti₃AlC₂ samples tested in supercritical water at 500 °C for 100 h [10]. Thus, any external stress will likely lead to extensive cracking and increased delamination.

4.3. Cr₂AlC

Electron microscopy and EDS analysis showed little observable change in the Cr₂AlC sample after autoclave testing. XRD analysis of the Cr₂AlC MAX phase was in agreement with this observation, showing no change in composition after testing and indicating that there was no formation of Al₂O₃. This finding is in contrast to the work by Lee et al. in high temperature (1300 °C) air testing of Cr₂AlC [9] where a protective Al₂O₃ layer was formed. It is postulated that a thin and protective chromia layer has formed during autoclave testing, which inhibits further oxidation of the bulk MAX phase. The protective oxide is very thin (between 5 to 10 nm) and appears to contain additions of Fe. The voids beneath the oxide layer are regions of Cr-depletion, believed to be due to the formation of the adjacent Cr oxide layer. Similar voids observed by Lee et al. were attributed to the depletion of Al to form an Al₂O₃ layer. Interestingly, Lee et al. observed oxygen ingress below the Al₂O₃ surface layer and in the present study, oxygen ingress is also observed below the Cr oxide after autoclave testing (Fig. 9). The corrosion resistance of Cr₂AlC in water is thus attributed to a dual oxide layer formation, comprised of an outer chromia layer and an inner alumina layer. This may be beneficial as the alumina may provide resistance to high temperature oxidation. A future study would be to pre-corrode Cr₂AlC and then expose it to high temperature air/steam to evaluate whether it is stable after autoclave testing.

5. Conclusions

The corrosion resistance of four different MAX phase compositions were tested in an autoclave using simulated primary water conditions. Cr₂AlC demonstrated the best corrosion resistance with minimal change from the pristine condition observed by EDS examination and no phase change observed during XRD investigation. The superior performance of Cr₂AlC is attributed to the high Cr content allowing the formation of passive chromia layer to form and thus inhibiting further oxidation. Although nano-scale void formation was observed in this MAX phase, it may not be detrimental to the use of Cr₂AlC in primary water applications. MAX phases relying on Si and/or Al as their passivating species produce no protective oxide during testing in primary water at 300 °C. The break-down of these oxides has been attributed to the preferential removal of A-layers and subsequent oxidation of the TiC layers has also been observed. A mechanism for the corrosion of these compositions has been proposed, which suggests such compositions are unsuitable for long-term use in the core of light-water reactors.

Acknowledgements

This work would not have been possible without the valuable discussions and support of Prof. Stuart Lyon regarding corrosion mechanisms. The author also recognises this research is funded by engineering and physical sciences research council (EPSRC) (EP/J021172/1, EP/1005420/1 and EP/M018563/1) and Rolls-Royce plc. The EELS experiments were performed at the SuperSTEM Laboratory, which is the UK National Facility for Aberration-Corrected STEM, supported by the EPSRC.

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