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# Nano-scale Si segregation and precipitation in $Cr_2Al(Si)C$ MAX phase coatings impeding grain growth during oxidation

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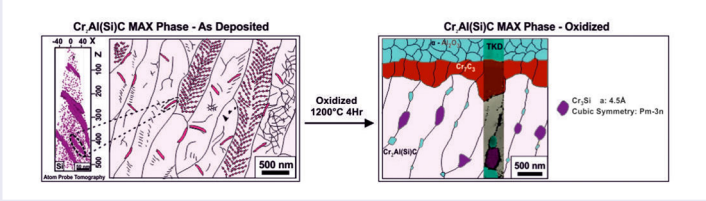
**ABSTRACT**

We recently reported that the columnar grain width of $Cr_2AlC$ MAX phase coatings increases during oxidation (4 h at 1120°C) by 80%, while for 0.7 at.% Si additions to $Cr_2AlC$, coarsening of only 12% was observed. Here, we use nm scale compositional and microstructural investigations to identify significant differences between $Cr_2AlC$ and $Cr_2Al(Si)C$. In particular, needle-shaped precipitates coarsen into globular $Cr_3Si$ precipitates upon oxidation in the Si-containing MAX phase. We infer that the presence of these precipitates, which are located predominantly along grain boundaries in the MAX phase, retards coarsening during oxidation by Zener pinning.

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**KEYWORDS**
MAX phases; self-healing; precipitate; grain boundary; Zener pinning

**IMPACT STATEMENT**

This is the first report of Zener pinning in MAX phases. We show that Si additions to $Cr_2AlC$ cause the formation of precipitates, which retard grain coarsening during oxidation.

## Introduction

$Cr_2AlC$ belongs to the subset of ternary metal carbides that have the general formula $M_{n+1}AX_n$ and are referred to as MAX phases (M: early transition metal; A: A group element; X: C or N) [1–3]. MAX phases typically exhibit nano-laminated structures with modulated charge density distributions, in which M-X layers (ionic - covalent bonds) are separated by A layers (metallic bonds). As a result, they possess both metallic and ceramic properties [1,2,4]. The potential for utilizing MAX phase ceramics (especially $Ti_3AlC_2$, $Ti_2AlC$ and $Cr_2AlC$) as self-healing materials has been investigated in recent years. In these materials, the products of oxidation, especially, $\alpha$-$Al_2O_3$ and other oxides have been shown to fill crack sites, thereby effectively healing them [5–8]. Song et al. [5] investigated the mechanical properties of the self-healed $Ti_3AlC_2$ MAX phase and reported that after oxidation, a crack-healed zone consisted primarily of $\alpha$-$Al_2O_3$, in addition to minor distributions of $TiO_2$. However, it was proposed that the formation of less protective and relatively weak $TiO_2$ needs to be avoided, in order to achieve better mechanical properties [5,9].

The quest for the development of self-healing MAX phase materials that produce only $\alpha$-$Al_2O_3$ along a crack zone after high temperature oxidation has directed research towards the study of $Cr_2AlC$ [10–14]. Yang et al. [8] investigated the oxidation kinetics of bulk $Cr_2AlC$ at 1100°C for 40 h. They reported that the diffusion of Al along oxide grain boundaries dominated the self-healing kinetics. These results suggest that $\alpha$-$Al_2O_3$ scale formation on $Cr_2AlC$ is comparable to that on other Al-containing high temperature materials, such as nickel and titanium aluminides [15]. However, the oxidation kinetics is sluggish. For efficient healing of macroscopic cracks, for example to impede erosive wear, fast crack healing and hence an increased oxidation rate are required.

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We recently showed that the addition of Si as a fourth alloying element in the minor amount of 0.7 at.% (determined by energy-dispersive X-ray spectroscopy (EDX)) to the $Cr_2AlC$ MAX phase can enhance the $Al_2O_3$ layer thickness by ~40% upon oxidation at 1120°C in air for 4 h [16,17]. It was also observed that the $Cr_2Al(Si)C$ MAX phase exhibited retarded grain growth during oxidation. Detailed near atomic-scale characterization using atom probe tomography (APT) did not reveal the presence of Si, even in trace amounts, either in the $Al_2O_3$ layer or in the chromium carbide layer located immediately below the $Al_2O_3$ layer. However, APT revealed the incorporation of up to $1.3 \pm 0.2$ at.% Si into the MAX phase after oxidation [16]. Hence, the role of Si in the retardation of MAX phase grain growth is currently not understood.

Here, we investigate the role of the addition of 0.7 at.% Si on phase formation and nanostructure evolution during annealing in the $Cr_2AlC$ MAX phase using Scanning Transmission Electron Microscopy (STEM), APT and Transmission Kikuchi Diffraction (TKD).

## Methods

MAX phases of $Cr_2AlC$ and $Cr_2Al(Si)C$ with 0.7 at.% Si were synthesized using DC magnetron sputtering in an industrial chamber (CC800/9, Cemecon AG, Germany). Further synthesis details can be found in Ref [16]. Oxidation was performed using a Carbolite HTF-1700 laboratory furnace at 1120°C for 4 h in air.

A probe-aberration corrected FEI Titan 80–200 transmission electron microscope equipped with in-column EDX detectors was used to record elemental distributions across different regions of the MAX phase coatings, both in the as-deposited and in the oxidized states. High-angle annular dark-field (HAADF) STEM images were recorded together with the EDX maps to correlate the structure and chemical composition. Further details about the microscope can be found in Ref. [18].

Sample preparation for STEM, TKD analysis, EDX mapping and APT was performed using an FEI Helios Nanolab 660 dual-beam system following the procedures that are described elsewhere [19–21]. APT tips were aligned along the growth direction of the as-deposited film. APT measurements were performed in laser-pulsed mode, with applied laser energy of 30 pJ at 250 kHz repetition rates, using a local electrode atom probe (LEAP 4000X HR) system from CAMECA Instruments. Tips were maintained at 60 K during the measurements. Data reconstruction and analysis were performed using IVAS 3.6.10a software.

TKD phase and orientation data were collected using an EDAX TEAM™ Pegasus EDS-EBSD system equipped with a HIKARI Plus electron backscatter diffraction detector. Analysis of the TKD-generated data was performed using EDAX OIM™ Analysis 8 software.

## Results and discussion

X-ray diffraction patterns recorded from the as-deposited $Cr_2AlC$ and $Cr_2Al(Si)C$ MAX phase samples indicate that phase-pure MAX phases were obtained for both compositions (Figure S1). The differences in

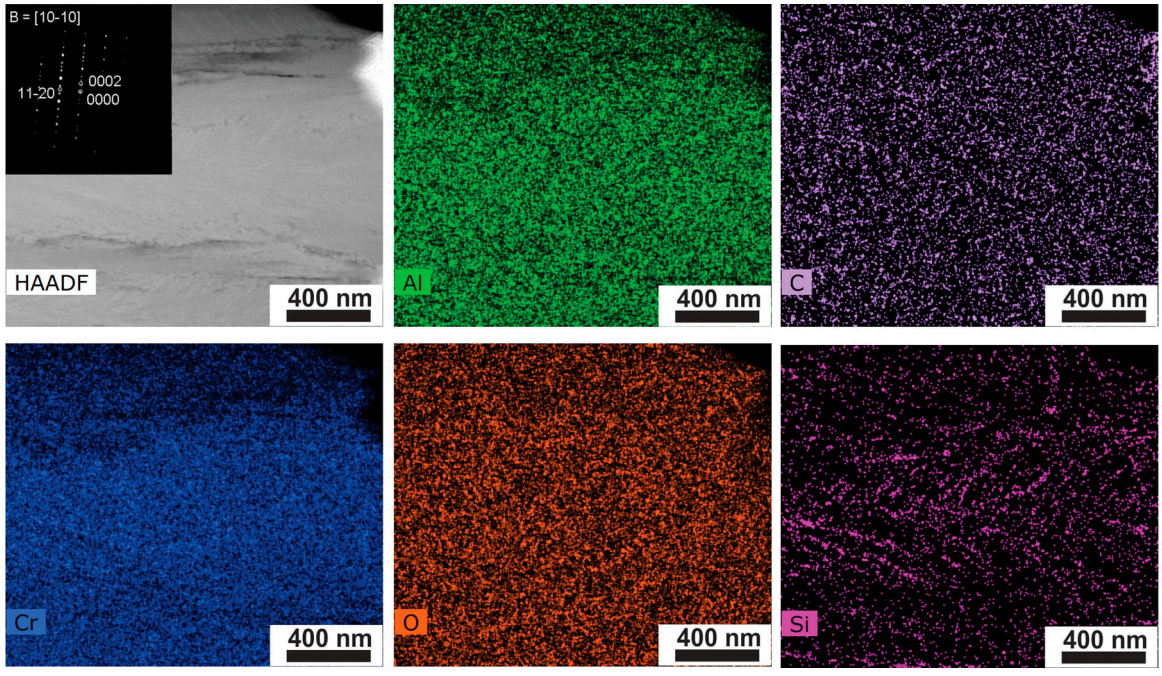


**Figure 1.** STEM-HAADF image of the as-deposited $Cr_2Al(Si)C$ MAX phase coating with an SAED pattern inset and corresponding elemental maps of Al, C, Cr, O and Si extracted from EDX measurement.

diffraction peak intensities corresponding to $Cr_2AlC$ and $Cr_2Al(Si)C$ indicate that both coatings grow with different textures.

Figure 1 shows the nanostructure and the elemental distribution of the $Cr_2Al(Si)C$ MAX phase in the STEM-HAADF image and corresponding EDX maps. Comparable to the $Cr_2AlC$ MAX phase sample (Figure S2), 'V shaped' defects are observed in the columnar MAX phase grains, with elemental maps of Cr, Al, C and O showing uniform and random distributions (see Figure 1). However, the Si distribution is non-uniform, with Si segregating to the 'V-shaped' defects. A selected-area electron diffraction (SAED) pattern (inset of Figure 1) recorded from a sample with an identical chemical composition to that reported in Ref. [16] was consistent with the formation of the $Cr_2Al(Si)C$ MAX phase.

In order to quantify the local composition of the segregated regions, APT measurements were performed on the same as-deposited $Cr_2Al(Si)C$ MAX phase sample as was utilized for the STEM/EDX investigations. Three-dimensional elemental distribution maps of each of the constituent elements along the growth direction of the film are shown in Figure S3. Si and O show strong local variations in concentration.

In order to analyse the spatial variation in the Si concentration further, a 10 at.% Si iso-concentration surface was used to distinguish between Si in the MAX phase matrix and the Si-enriched needle-shaped regions, as shown in Figure 2. A proximity histogram obtained from interface 1 indicates the presence of a ~10 nm thick precipitate with approximate composition $Cr_5Si_3C$. In contrast, a proximity histogram obtained from interface 2 indicates the presence of a ~5 nm thick precipitate with approximate composition $Cr_3Si$. The minimum length of the precipitates is on the order of 250 nm, although it should be taken into consideration that the APT tip volume is limited. It can also be inferred from the proximity histograms that Si shows a solubility of up

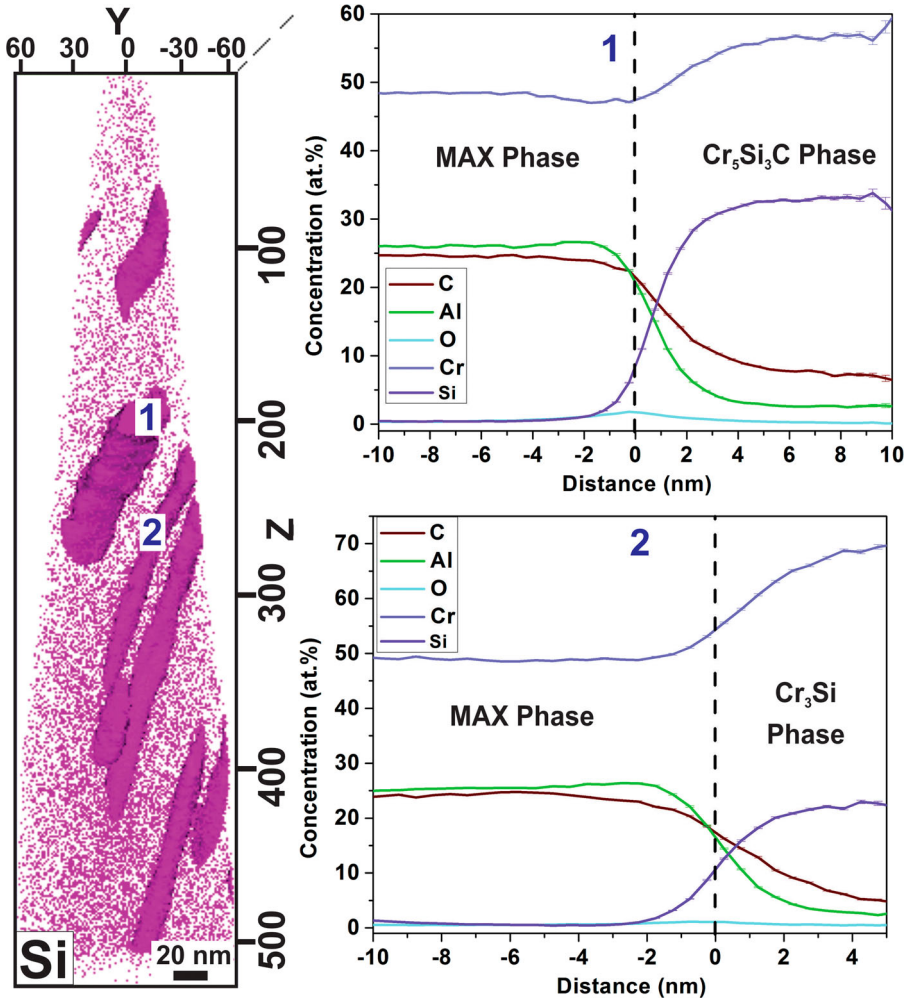


**Figure 2.** Three-dimensional elemental distribution map of Si in the as-deposited $Cr_2Al(Si)C$ MAX phase coating, with the Si-enriched regions delineated by a 10 at.% isoconcentration surface. Proximity histograms taken along interfaces 1 and 2 using a 0.5 nm bin width are shown on the right.

to 0.5 ± 0.02 at.% in the MAX phase matrix. It should be noted that the formation of segregations (identified using STEM-EDX in Figure 1) and precipitations (identified using APT in Figure 2 and S3) is not reflected in the XRD data (Figure S1). Although the segregations may or may not be crystalline, the volume fraction of the precipitations may be too small to be detected using XRD (assuming that they are crystalline). Furthermore, no positive phase identification of the precipitates could be obtained using SAED [16]. The Si rich precipitations, which have a thickness of ∼5–10 nm and a length on the order of 250 nm, should be visible using TEM and hence should be detectable using SAED. Furthermore, the observation of trace Si segregation along the 'V shaped' defect sites in Figure 1, without appreciable Cr or C enrichment, suggests that these segregations are different to the precipitations observed using APT (with Cr or C enrichment). It may therefore be speculated that preferential FIB milling of these precipitations (possibly along grain boundaries) occurred during TEM specimen preparation, thereby excluding them from SAED diffraction analysis. Evidence in support of this hypothesis is provided by the observation of 50–80 nm wide and 800 nm – 2 µm long regions of material loss (continuous void formation) along specific grain boundary regions from the TEM lamella used for imaging the as-deposited $Cr_2Al(Si)C$ MAX phase sample (see Figure 5 in Ref. [16]). The size (50–80 nm wide) of these regions approximately resembles the size of the precipitates observed in Figure 2 and Figure S3.

In an effort to image Si segregations and Si precipitations in one sample, STEM imaging and EDX mapping were performed on an APT tip prepared from the as-deposited $Cr_2Al(Si)C$ MAX phase sample, as shown in Figure S4. The STEM HAADF image shows contrast variations that may be, at least in part, due to variations in atomic number (Z) of the (segregated) elements that are present in the imaged volume. In addition to Z-contrast, diffraction contrast arising from the potentially nanocrystalline nature of the sample may be present. Corresponding EDX elemental maps reveal a Si distribution that is similar in morphology (thickness and length) to the Si-rich precipitations observed using APT in Figure 2.

It should be noted that the impurity O concentrations in both the Si rich precipitations and the matrix MAX phase regions, as observed in the proximity histograms shown in Figure 2, are $\leq$ 0.44 ± 0.01at. %. The local O enrichment seen in Figure S3 corresponds to enrichment in O up to a concentration of 1.12 ± 0.02 at.% at the interface between the Si-rich precipitates and the MAX phase, as observed in the proximity histograms shown in Figure 2. Interestingly, such O segregation is not observed in the $Cr_2AlC$ MAX phase sample, even along the 'V-shaped' defects in Figure S2.

Hence, no segregation or significant spatial distribution in chemical composition could be identified in the $Cr_2AlC$ coating. However, the Si-containing films exhibit Si segregations and precipitations, as discussed above. It was previously observed that a $Cr_2Al(Si)C$ MAX phase

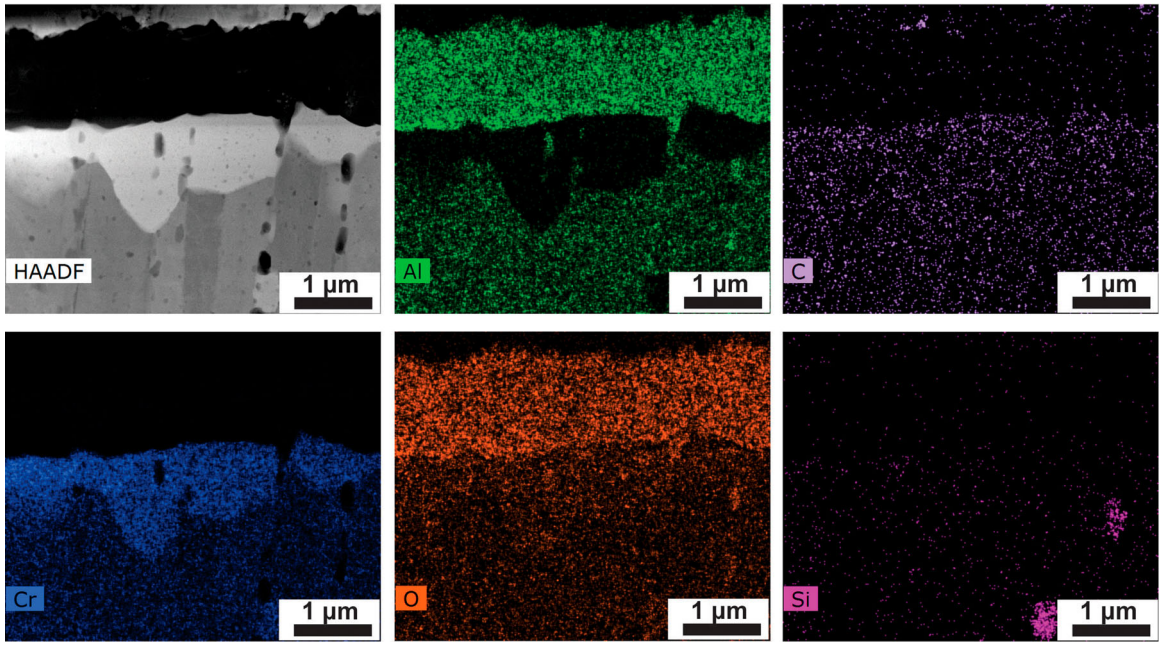


**Figure 3.** STEM-HAADF image of the 1120°C 4 h oxidized $Cr_2Al(Si)C$ MAX phase and corresponding elemental maps of Al, C, Cr, O and Si extracted from EDX measurement.

retarded grain growth during oxidation at 1120°C for 4 h in air [16]. In order to obtain a comparison with the as-deposited state, STEM-EDX analysis was performed on the oxidized $Cr_2Al(Si)C$ MAX phase sample, as shown in Figure 3. The presence of $Al_2O_3$ and $Cr_7C_3$ layers can be inferred from the observed enrichment of Al and Cr in the elemental maps. The absence of Si in these layers is consistent with previously reported APT observations [16].

In contrast to the as-deposited state, distinct regions where Al and Si are separately enriched can be observed along the grain boundaries of the parent MAX phase. The Al-enriched regions are associated with an increased O concentration. Hence, these local precipitations along the grain boundaries appear to be alumina. It is reasonable to assume that the formation of $Al_2O_3$ particles along the MAX phase grain boundaries is a consequence of O inward diffusion during the oxidation process [8] and diffusion of O that was incorporated from the residual gas during sputtering [22]. Similarly, the regions that are enriched in Si are also located along the grain boundaries and are characterized by an increase in Cr concentration.

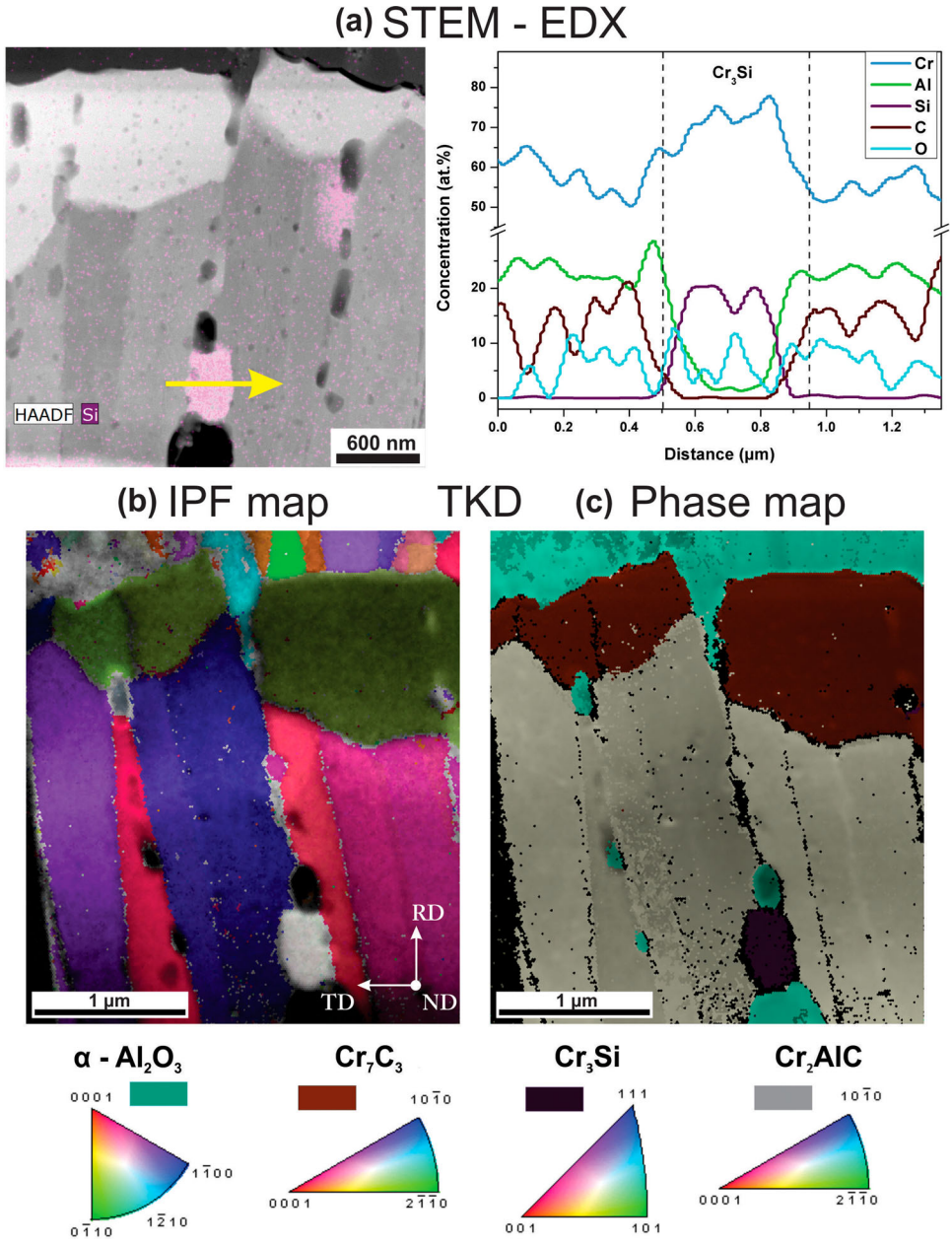


**Figure 4.** Correlative analysis of the 1120°C 4 h oxidized $Cr_2Al(Si)C$ MAX phase coating (a) STEM-HAADF image overlaid with the Si elemental map and corresponding 1-dimensional concentration profile taken along the Si-rich precipitate indicated by the yellow arrow. (b) Transmission Kikuchi diffraction inverse pole figure map and (c) the corresponding phase map showing the presence of cubic $Cr_3Si$ precipitates along the hexagonal-close-packed MAX phase grain boundaries.

When compared with the local composition analysis carried out on the as-deposited samples, the needle-shaped precipitations have coarsened significantly (from ~5–10 nm in diameter in the as-deposited state) to domains of ~500 nm in diameter. A 1-dimensional concentration profile obtained along a Si-rich precipitate (indicated by a yellow arrow in Figure 4(a)) is consistent with a $Cr_3Si$ stoichiometry. In order to complete the investigation of the local composition with structural information, correlative TKD measurements were performed on the same sample that was used for STEM-EDX mapping (Figure 3). The results are shown in Figure 4(b) and (c). The microstructure of the oxidized $Cr_2Al(Si)C$ MAX phase sample along the cross-section is shown in the form of a map that indicates the crystallographic direction normal to the thin film and the oxide scale growth directions using inverse pole figure (IPF) colors in Figure 4(b). In the phase map shown in Figure 4(c), columnar MAX phase grains, which have a column diameter of ~100–300 nm, are visible under a ~700 nm thick $Cr_7C_3$ layer and the $\alpha$-$Al_2O_3$ layer. A cubic $Cr_3Si$ globular precipitate phase (a = 4.5 Å; purple color) is visible along the columnar MAX phase grain boundary.

Based on the measurement of local composition and microstructure presented above, a schematic representation of the oxidation-induced changes in morphology of $Cr_2AlC$ and $Cr_2Al(Si)C$ is shown in Figure 5. Significant coarsening is observed for the $Cr_2AlC$ MAX phase grains [16] after oxidation for 4 h at 1120°C. For the Si-containing $Cr_2AlC$, coarsening is retarded [16]. Based on the observation of Si segregation at 'V-shaped' defects and the presence of Si-rich precipitates with approximate compositions $Cr_3Si$ and $Cr_5Si_3C$ located along grain boundaries, we infer that these precipitations hinder grain growth by Zener pinning. The grain boundary mobility of the $Cr_2Al(Si)C$ MAX phase sample appears to be significantly reduced due to the presence of the Si-rich precipitations, resulting in retarded coarsening.

In order to further elucidate the effect of Zener pinning on MAX phase grain growth, the temporal evolution of the 1 at.% Si containing $Cr_2AlC$ MAX phase columnar width during oxidation in air at 1100°C for up to 240 min is compared with Si free $Cr_2AlC$ MAX phase. The corresponding results are displayed in Figure 6, where it is shown that the addition of 1 at.% Si to $Cr_2AlC$ MAX phase retards grain growth significantly compared

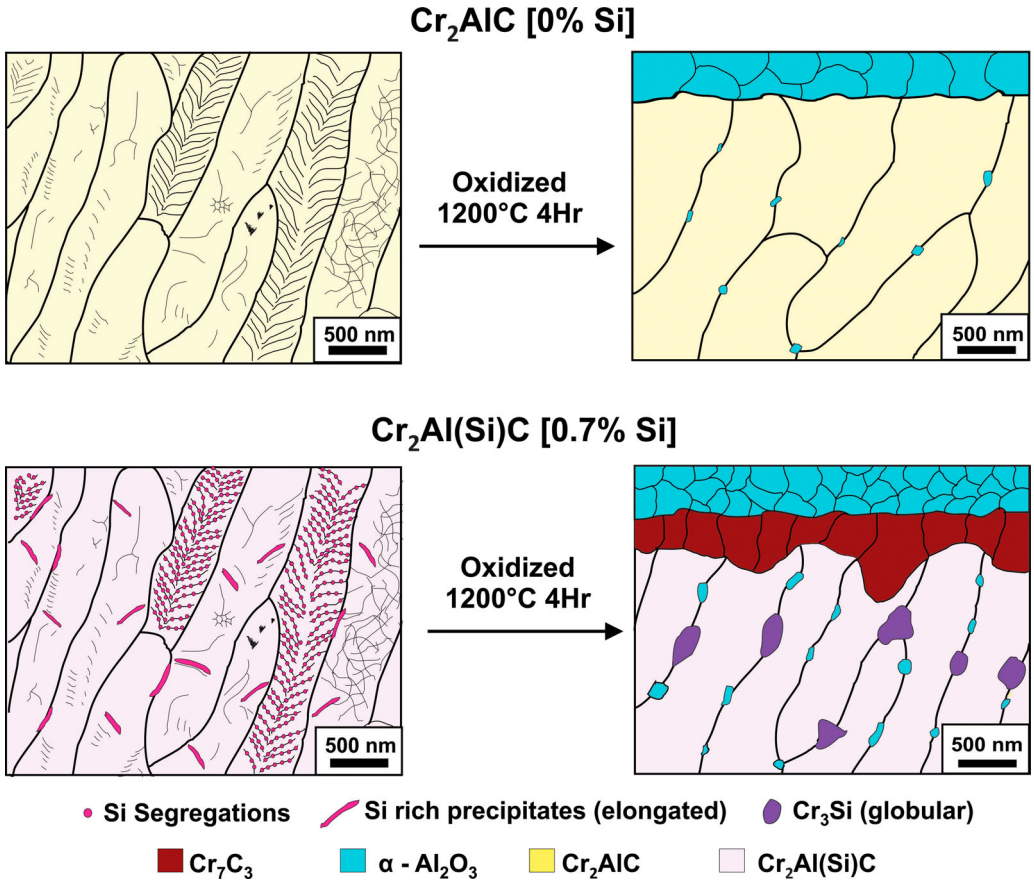


**Figure 5.** Schematic representations of oxidation-induced changes in the morphology of the $Cr_2AlC$ and $Cr_2Al(Si)C$ coatings. The as-deposited morphologies are compared to those obtained after oxidation for 4 h at 1120°C.

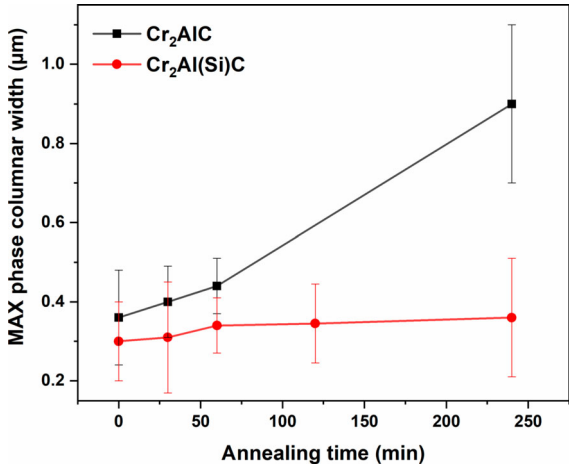


**Figure 6.** Variation in columnar grain width as a function of annealing time for $Cr_2AlC$ and 1 at.% Si added $Cr_2Al(Si)C$ MAX phases annealed at 1100°C in air.

to the Si free $Cr_2AlC$ MAX phase. These data underline that Zener pinning defines the high temperature behavior of Si containing MAX phases during high temperature exposure.

## Conclusions

We have studied phase formation and nanostructure evolution in as-deposited and oxidized (at 1120°C for 4 h in air) MAX phase samples of $Cr_2AlC$ and 0.7 at.% Si containing $Cr_2Al(Si)C$. Si was observed to segregate at 'V-shaped' growth defects in the MAX phase grains, in addition to being incorporated in the form of $Cr_3Si$ and $Cr_5Si_3C$ needle-shaped precipitations, which are located preferentially along grain boundaries in the as-deposited $Cr_2Al(Si)C$ MAX phase. Upon oxidation at 1120°C for 4 h in air, the needle-shaped (~5–10 nm diameter) $Cr_3Si$ precipitates were observed to undergo significant coarsening into a globular morphology (~500 nm in diameter), accompanied by annihilation of the Si-enriched 'V-shaped' growth defects. TKD measurements confirmed the presence of cubic $Cr_3Si$ (a = 4.5 Å) precipitates along the grain boundaries of the Si-containing MAX phase. In comparison to the $Cr_2AlC$ MAX phase (without Si additions) which shows an 80% increase in columnar grain width upon oxidation, coarsening of the $Cr_2Al(Si)C$ MAX phase upon oxidation was retarded to only 12%. This difference by a factor of 6.7 in the coarsening behavior is attributed to Zener pinning of grain boundaries by the Si-containing precipitates.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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