

Synthesis and Oxidation Testing of MAX Phase Composites in the Cr–Ti–Al–C Quaternary System

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According to the properties determined for the ternary end-members, MAX phases in the quaternary Cr–Ti–Al–C system could be of interest as protective coatings for nuclear fuel cladding in the case of severe accident conditions. In this study, syntheses of 211 and 312 MAX phase compositions were attempted using pressureless reactions starting from Cr, TiH₂, Al, and C (graphite) powders. It was observed that both the Ti substitution by Cr in Ti₃AlC₂ and the mutual solubility of Ti₂AlC and Cr₂AlC are limited to a few atomic percent. In addition, the remarkable stability of the (Cr_{2/3}Ti_{1/3})₃AlC₂ MAX phase composition was confirmed. Due to the low miscibility of MAX phases in the Cr–Ti–Al–C system, most samples contained substantial amounts of TiC_x and Al–Cr alloys as secondary phases, thus forming composite materials. After sintering, all samples were submitted to a single oxidation test (12 h at 1400°C in air) to identify compositions potentially offering high-temperature oxidation resistance and so warranting further investigation. In addition to (Cr_{0.95}Ti_{0.05})₂AlC, composite samples containing substantial quantities of Al₈Cr₅ and AlCr₂ formed a stable and passivating Al₂O₃ scale, whereas the other samples were fully oxidized.

I. Introduction

Cr₂AlC, Ti₂AlC, and Ti₃AlC₂ are ternary layered carbides belonging to the MAX phase family. These compounds crystallize with the hexagonal P6₃/mmc structure and respecting the formula M_{n+1}AX_n, with $n = 1, 2,$ or 3 , where M is an early transition metal, A is a group 13–16 element and X is carbon and/or nitrogen.¹ When $n = 1$, the MAX phase is a 211-type, for $n = 2$, 312-type and for $n = 3$, 413-type. In the past 20 years, after Barsoum and El-Raghy reported the remarkable properties of Ti₃SiC₂² and the subsequent confirmation that most of Ti₃SiC₂ properties are shared by all the other MAX phases,^{3,4} there has been a growing research interest in them. The main characteristic of the MAX phases, which also explains their remarkable properties, is their structure, composed of the stacking of n “ceramic” M–X planes interposed with a “metallic” A layer. Thanks to this, the MAX phases exhibit, like most ceramics, high decomposition temperature and elastic stiffness, but they

also possess, like metals, a high thermal shock resistance, high thermal and electrical conductivities, and good machinability.

Kinetics and regimes of oxidation of MAX phases in air at high-temperature are sensitive to chemical composition, including levels of impurities. This is because MAX phases are easily oxidized and their operational oxidation resistance is experimentally driven by the nature and properties of the oxide(s) outer scale(s) formed during the first stages of oxidation.¹ Among the known MAX phases, Cr₂AlC and Ti₂AlC followed by Ti₃AlC₂ have been reported to have the best oxidation resistance in air due to the formation of a passivating Al₂O₃ outer scale.^{1,5–8} Their operational temperature limit in air for prolonged times (few months) is at least 1300°C.^{1,5–8} The oxidation mechanisms of Ti₂AlC and of Ti₃AlC₂ have been extensively studied.^{6–14} Usually, a thin (1–3 μm) TiO₂ outer layer is formed onto a dense, adherent and therefore protective Al₂O₃ scale (10–40 μm). Tallman et al.⁵ demonstrated by re-plotting various published results of Ti₂AlC and Ti₃AlC₂ high-temperature oxidation that oxidation kinetics and thereby Al₂O₃ scale thickening obey cubic laws. Moreover, it is worth mentioning the well-matched thermal expansion coefficients (CTE) between Al₂O₃¹⁵ and Ti₂AlC¹⁶ which minimizes the thermal residual stresses. As a result, Ti₂AlC is not susceptible to spallation during thermal cycling^{1,5,17} and its upper continuous use temperature is about 1450°C, above such temperature Al₂TiO₅ formation induces cracking in the Al₂O₃ scale.¹² On the other hand, Cr₂AlC has a more peculiar oxidation behavior, due to the formation of an alumina layer over a chromium carbide (Cr₃C₇) underlayer.^{1,5,8,18–22} The formed carbide is thought to be a consequence of the higher difference of Al and Cr outward diffusion kinetics in Cr₂AlC compared to the other carbide MAX phases. Unlike Ti₂AlC, Cr₂AlC possesses a high thermal expansion coefficient^{23,24} that provokes cracks and spallation of the outer scales over 1200°C after prolonged times.^{1,22}

Because of the above mentioned properties, some of the MAX phases have potential to be used as passive safety protection of nuclear fuel cladding in the eventuality of a severe accident (for accidental scenarios such as that which occurred at Fukushima in 2011). Specifically, the industrial need for the Accident-Tolerant Fuel (ATF) concept is, at minimum, to provide protection against oxidation of the fuel cladding material (a Zr-based alloy) for a few tens of hours at temperatures over 1200°C.²⁵ Cr₂AlC, Ti₃AlC₂, and Ti₂AlC are therefore considered excellent candidates regarding the first major requirement (oxidation resistance) but they also comply with the second major requirement, having a low neutron

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absorption cross section. This parameter is of great importance because a highly neutron-absorbing material would lower the reactor performance in normal operating conditions and therefore lower its cost-effectiveness. Also, a lower neutron cross section is usually accompanied by limited activation, simplifying and reducing the cost of waste management. Hoffmann et al.²⁶ have proven by calculations Ti₂AlC has reasonable performance regarding neutron absorption and material activation. Given the low neutron cross sections of natural Cr isotopes and of their different activation products,²⁷ use of Cr would not be problematic either.

To the best of our knowledge, only a few works exist on the synthesis of Cr–Ti–Al–C MAX phases and only one on oxidation behavior. In 1980, Schuster et al. identified MAX phases in the Cr–Ti–Al–C system.²⁸ These reacted with mixtures of Cr₂AlC and Ti₂AlC in various proportions under vacuum at 1000°C for 170 h. They estimated to reach about 6 at.% maximum solubility of Cr in Ti₂AlC and around 25 at.% substitution of Cr by Ti in Cr₂AlC. More recently, Kim et al.²⁹ synthesized Cr-rich mixed *211* MAX phases (substitution rate of 5, 10 and 20 at.% of Cr by Ti). Based on their X-ray diffraction (XRD) analysis, they achieved targeted solid solutions up to 10 at.% substitution while secondary phases formed for the 20 at.% synthesis. They concluded the incorporation limit of Ti in Cr₂AlC lies between 10 and 20 at.% of substitution, in conflict with the value reported by Schuster et al.²⁸ Further recent work by Lee et al.^{21,30} focused on (Cr_{0.95}Ti_{0.05})₂AlC in comparison to similarly prepared Cr₂AlC (hot-pressed at 25 MPa and 1250°C for 1 h from CrC_x, TiC_x, and Al powders). They determined that the addition of Ti, even limited to 5 at.% substitution of Cr had a notable negative impact on oxidation resistance in the 700°C–1100°C range. This was attributed to the local formation of TiO₂ nodules in the Al₂O₃ scale, impairing its passivating nature. In 2014, Ying et al.³¹ attempted to synthesize (Cr,Ti)₂AlC MAX phases using SHS (Self-propagating High-temperature Synthesis) with Cr/(Ti+Cr) ratios from 0.125 to 0.75. XRD revealed Cr₂AlC and/or Ti₃AlC₂-like phases as the only MAX phase components in all the composites produced (TiC, Al₈Cr₅, and AlCr₂ composing the other crystalline phases). Unfortunately they did not discuss Cr incorporation in Ti₃AlC₂ and conversely Ti incorporation in Cr₂AlC. Also recently, Liu et al.^{32,33} synthesized and identified two new MAX phases: (Cr_{2/3}Ti_{1/3})₃AlC₂ and (Cr_{5/8}Ti_{3/8})₄AlC₃. This is remarkable since among the end-members of these two MAX phase solid solutions, only Ti₃AlC₂ has been experimentally identified. The authors also tried various Cr/(Cr+Ti) ratios and obtained in all cases the exact same MAX phase along with other compounds accommodating the element(s) in excess. They attributed the formation and higher stability of the precise (Cr_{2/3}Ti_{1/3})₃AlC₂ composition to the ordering of two M elements onto the two different M Wyckoff sites in *312* MAX phases: the *4f* site hosting 2/3 of the M element (here Cr) and the *2a* site the remaining 1/3 (Ti).³³ This was the first report of M ordering in (MM')₃AX₂ MAX phases, before Caspi et al.³⁴ and Anasori et al.³⁵ demonstrated it in (Cr_{0.5}V_{0.5})₃AlC₂ and (Mo_{2/3}Ti_{1/3})₃AlC₂, respectively.

To further investigate mixed Ti₂AlC–Cr₂AlC compounds, the first part of this work reports attempts to synthesize five targeted mixed-compositions: (Cr_{0.05}Ti_{0.95})₂AlC, (Cr_{0.25}Ti_{0.75})₂AlC, (Cr_{0.50}Ti_{0.50})₂AlC, (Cr_{0.75}Ti_{0.25})₂AlC, and (Cr_{0.95}Ti_{0.05})₂AlC, hereafter denoted as *211-Cr5Ti95*, *211-Cr25Ti75*, *211-Cr50Ti50*, *211-Cr75Ti25*, and *211-Cr95Ti5* samples, respectively. These were tentatively prepared by reaction of elemental powders, followed by SPS (Spark Plasma Sintering). As the initial results from this first batch showed the favorable formation of *312*-type MAX phases solid solutions, the initial study was extended to attempts to synthesize purer *312* phases using more suitable starting powder mix compositions, with targeted compositions (Cr_{0.05}Ti_{0.95})₃AlC₂, (Cr_{1/3}Ti_{2/3})₃AlC₂, (Cr_{0.50}Ti_{0.50})₃AlC₂, and

(Cr_{2/3}Ti_{1/3})₃AlC₂, hereafter noted *312-Cr5Ti95*, *312-Cr1/3Ti2/3*, *312-Cr50Ti50*, and *312-Cr2/3Ti1/3*, respectively. Finally, oxidation resistance at high temperature of all the prepared samples was evaluated by a 12 h exposure test to air at 1400°C to identify potential compositions of interest for ATF.

II. Experimental Procedure

Commercial reactants used were TiH₂ (>99%, ~40 μm), Cr (>99.95%, <75 μm), Al (~40 μm, >99.5%), all provided by Alfa Aesar, and graphite (>99.9%, <20 μm) purchased from Sigma-Aldrich (Dorset, UK). Taking into account the risks associated with handling fine metallic powders and also to limit oxygen contamination, mixtures preparations were done under argon in a glove box. Reactants were mixed by 30 minutes ball-milling (Nanjing University Instrument Plant) in Nylon jars using zirconia balls (diameter-10 mm). The jars and balls were “washed” prior to use by 30 minutes milling with a few grams of the main Ti or Cr reactant followed by a new milling step with ethanol. As is the custom for Al-based MAX phase synthesis, stoichiometries were experimentally adjusted to 2/1.05/0.95 (for *211* systems) and to 3/1.1/0.9 (for *312* systems) for Ti+Cr, Al and C, respectively. This aimed to compensate for the partial sublimation of Al occurring between Al melting and its reaction with graphite to form Al₄C₃ and to account for the partial carbon uptake resulting from the contact with the graphite crucibles and SPS dies and/or the usual substoichiometry in element X in MAX phases, as reported, for example, for Ti₃AlC₂.³⁶

Synthesis and sintering were performed using two separate heat treatments. Synthesis was performed in graphite crucibles lined and capped with graphite paper. For *211* syntheses, heat treatment consisted of 10 h at 1300°C under Ar with heating and cooling rates of ~20°C/min. The 1300°C synthesis condition was selected as a compromise to allow good *211* MAX phase formation based on literature data^{21,28,30,37–39} while trying to limit Ti₃AlC₂ formation which is known to form at 1350°C–1450°C from Ti₂AlC and remnant TiC.⁴⁰ For *312* systems, the maximum temperature was raised to 1450°C and maintained for 1 h to comply with what is usually necessary to form Ti₃AlC₂.^{36,41,42} For the pressureless synthesis, the used furnace was a FCT Systeme HP W/25/1, Rauenstein, Germany. Depending on the hardness of the obtained solids, these were simply manually ground in an agate mortar with a pestle and sieved <250 μm (all *312* syntheses), or ball-milled for 4 h in the same jars used for powder mixing (*211-Cr95Ti5* and *211-Cr75Ti25*) and sieved <250 μm or hammered between hard stainless steel or Ti₃SiC₂ blocks and sieved <800 μm (*211-Cr50Ti50*, *211-Cr25Ti75*, and *211-Cr5Ti95*). Sintering was then achieved by SPS using a HP D/25/1 FCT Systeme equipment and 30 mm graphite cylindrical mold jacketed with graphite paper. Optimized thermal and pressure cycles employed for both the *211* and *312* samples were the following: pressing at 5 kN (7 MPa); heating at 300°C/min to 950°C; heating at 100°C/min to 1050°C while progressively increasing the applied pressure to 24.7 kN (35 MPa); heating at 300°C/min to 1220°C and 10 minutes plateau; cooling at 300°C/min to 950°C with release of pressure to 5 kN between 1050°C and 950°C; natural cooling to room temperature.

XRD was performed with a Bruker D2 Phaser SSD160 (Karlsruhe, Germany) using a 0.03° 2θ step and an angular range of 5° to 105° 2θ. Crystalline phase determination was done with the help of Xpert High Score Plus software (PANalytical, Almelo, the Netherlands) using ICDD (International Center for Diffraction Data) database. Refinement of unit cell parameters was done by full-pattern matching (Le Bail function) using Fullprof Suite program.⁴³ A second refinement was also done by the Rietveld method to determine the volume ratio of each crystalline phase. Cross section and fracture surface characterizations were performed using a JEOL JSM-6400 (Tokyo, Japan) SEM equipped with

a BSE (Back-Scattered Electron), a SE (Secondary Electron) and an EDX detector (ultra-thin polymer window, INCA; Oxford Instruments, Oxford, U.K.). For resin-embedded samples, a ~10 nm gold coating was applied to ensure electrical conductivity.

Oxidation tests were performed by placing 1200 grit polished coupons of ~1 cm × 0.5 cm × 0.5 cm of the sintered pellets into a self-ventilated furnace heated at 10°C/min to 1400°C and held at this temperature for 12 h.

III. Results and Discussion

(1) Characterization of 211 Targeted Compounds

Figure 1 shows the X-ray diffractograms of the five 211 samples after sintering. It has to be noted that sintering by SPS at 1220°C has, from XRD point of view, no influence on the samples since very similar diffractograms were obtained before sintering (thus after 1300°C pressureless reaction of starting reactants).

From XRD, *211-Cr95Ti5* is almost a monophasic 211 MAX phase; the only detected crystalline impurity being a Al–Cr alloy. SEM characterization [Figs. 2(a) and (b)] agrees well with XRD as the predominant microstructure of fractured *211-Cr95Ti5* sample is a lamellar microstructure, typical of MAX phases. EDX analysis confirms the predominant and homogeneous formation of $(\text{Cr}_{0.95}\text{Ti}_{0.05})_2\text{AlC}$ as the expected Cr/Ti/Al ratios are obtained. EDX and BSE also outline the minor presence of Al–Cr alloys (in agreement with XRD) and of TiC. The determined unit cell parameters for $(\text{Cr}_{0.95}\text{Ti}_{0.05})_2\text{AlC}$ (Table I) can be compared to accurate (i.e., post-80°) reported values for Cr_2AlC ($2.844 \leq a \leq 2.865 \text{ \AA}$ and $12.814 \leq c \leq 12.857 \text{ \AA}$ ^{23,29,44–47}). As expected from the larger atomic radii of Ti, partial substitution of Cr by Ti causes an expansion of the unit cell parameters. More interestingly, the unit cell volume ($V = 91.57(5) \text{ \AA}^3$) lies exactly where expected when assuming a Vegard's law relation between Cr_2AlC ($V = 90.71 \text{ \AA}^3$)^{3,23,29,44–47} and Ti_2AlC ($V = 110.71 \text{ \AA}^3$)^{16,47–52}.

As revealed in Fig. 1, an increase in titanium content in *211-Cr75Ti25* leads to the formation of very different crystalline phases. Three non-MAX phases were found: TiC, Al_8Cr_5 , and AlCr_2 . These three phases were the most common among the untargeted phases observed in the present work. It has to be noted that from this point onward, these compositions will be used although it is probable that TiC_x contains some Cr in partial substitution of Ti (up to 3.5 wt% as determined by Guha and Kolar⁵³) and conversely Al_8Cr_5 and AlCr_2 can contain some Ti (up to 6.2 and 2 at.%, respectively, according to Raghavan⁵⁴) and/or C. Unexpectedly,

a 312 MAX phase (M_3AlC_2) was formed as the main crystalline phase in *211-Cr75Ti25*. This is confirmed by SEM/EDX [Figs. 2(c) and (d)] as about half of the microstructure appears laminated (MAX phase) and half exhibits rounded polycrystalline features. EDX spot analyses for the lamellar grains an Al/(Al+Cr+Ti) atomic ratio of $28\% \pm 6\%$ (12 independent measurements), close to the value of 25% for $(\text{Cr,Ti})_3\text{AlC}_2$. Furthermore, the same spot analyses gave Cr/(Ti+Cr) ratio of $61\% \pm 8\%$. Refinement of the XRD data for the 312 MAX phase produced unit cell parameters of $a = 2.935(1) \text{ \AA}$ and $c = 17.894(7) \text{ \AA}$. These values are close to those reported by Liu et al.³² for $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ ($a = 2.921 \text{ \AA}$ and $c = 17.878 \text{ \AA}$). Thus, all results strongly suggest that the obtained 312 MAX phase is $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$. Rietveld analysis (Table I) showed the composite produced is composed of ~40% $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$, ~20% TiC and ~40% Al–Cr alloys.

The same undesired phases observed in *211-Cr75Ti25* are found by XRD in *211-Cr50Ti50*. However, the *211-Cr50Ti50* sample also contains a Cr-rich 211 MAX phase. The phase composition of the composite produced (Table I) is similar to that of Ying et al. who were targeting the same MAX phase using SHS.³¹ Figures 2(e) and (f) show the sample is composed of fine grains ($\leq 2 \mu\text{m}$) precluding proper EDX characterization. The determined unit cell parameters (Table I) confirms this phase is Cr-rich compared to the Cr/(Cr+Ti) targeted ratio. Furthermore, these values are close to those determined for *211-Cr95Ti5*. This result thus suggests Ti incorporation in Cr_2AlC should be limited to a Ti/(Cr+Ti) ratio of ~5%.

211-Cr25Ti75, according to XRD, is also mainly composed of a 312 MAX phase, along with TiC, Al_8Cr_5 , and AlCr_2 . SEM [Figs. 2(g) and (h)] explicitly shows that the MAX phase microstructure is predominant (Table I). Lattice parameters determined (Table I) are very different to those determined for the 312 phase found in *211-Cr75Ti25* but are close to those usually reported for Ti_3AlC_2 ($3.065 \leq a \leq 3.0786 \text{ \AA}$ and $18.487 \leq c \leq 18.73 \text{ \AA}$ ^{36–42,55,56}). As a consequence the obtained 312 MAX phase should have a limited amount of Cr in its structure. This is corroborated by the presence of Al_8Cr_5 and AlCr_2 phases, which presumably contain most of the excess chromium. More importantly, EDX point measurements indicated that the Cr/(Cr+Ti) ratio in the 312 MAX phase grains is $2\% \pm 2\%$. Also, this result is comparable to Ying et al.'s attempt to synthesize³¹ $(\text{Cr}_{0.75}\text{Ti}_{0.25})_2\text{AlC}$ by SHS as they determined their composite to be composed of predominantly Ti_3AlC_2 and TiC with minor Cr_2AlC and Al_8Cr_5 .

Finally *211-Cr5Ti95* is, according to XRD (Fig. 1) and SEM/EDX [Figs. 2(i) and (j)], a mixture of a 211 and a 312 MAX phase, along with TiAl_2 and CrAl_2 present as minor phases. The lattice parameters obtained for the 211 and 312 phases are close to those reported for Ti_3AlC_2 ^{36–42,55,56} and Ti_2AlC ,^{16,23,24,47–52} respectively, suggesting incorporation of Cr in both MAX phases should be very limited. EDX characterization agrees well with that as the Cr/(Cr+Ti) ratio is $2\% \pm 1\%$ for both phases.

In this first set of experiments, *211-Cr95Ti5* and *211-Cr5Ti95* were found to lead to the formation of MAX phases almost exclusively, with *211-Cr95Ti5* leading to the targeted $(\text{Cr}_{0.95}\text{Ti}_{0.05})_2\text{AlC}$ composition, whereas *211-Cr5Ti95* is a mixture of $(\text{Cr}_{0.02}\text{Ti}_{0.98})_2\text{AlC}$ and $(\text{Cr}_{0.02}\text{Ti}_{0.98})_3\text{AlC}_2$. In agreement with previous work,^{21,28–32} mutual solubility of Ti_2AlC and Cr_2AlC is found limited to few atomic percent with Cr_2AlC being a better host for Ti than the other way around. As a consequence intermediate compositions (*211-Cr25Ti75*, *211-Cr50Ti50*, and *211-Cr75Ti25*) contain substantial amounts of undesired phases along with, respectively, slightly Cr-doped Ti_3AlC_2 , slightly Ti-doped Cr_2AlC and $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$. In light of this last finding, new powder batches aiming at the synthesis of 312 MAX phases were subsequently prepared and are discussed in the next section.

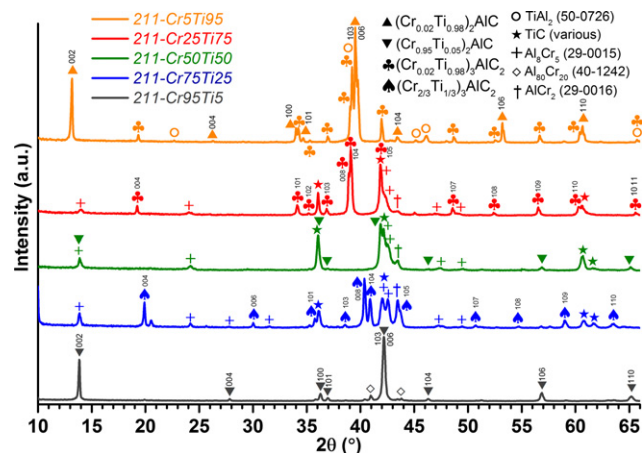


Fig. 1. X-ray diffractograms of 211 samples. Determination of crystalline phases was made using ICDD database and matched datasheet numbers are indicated in parentheses.

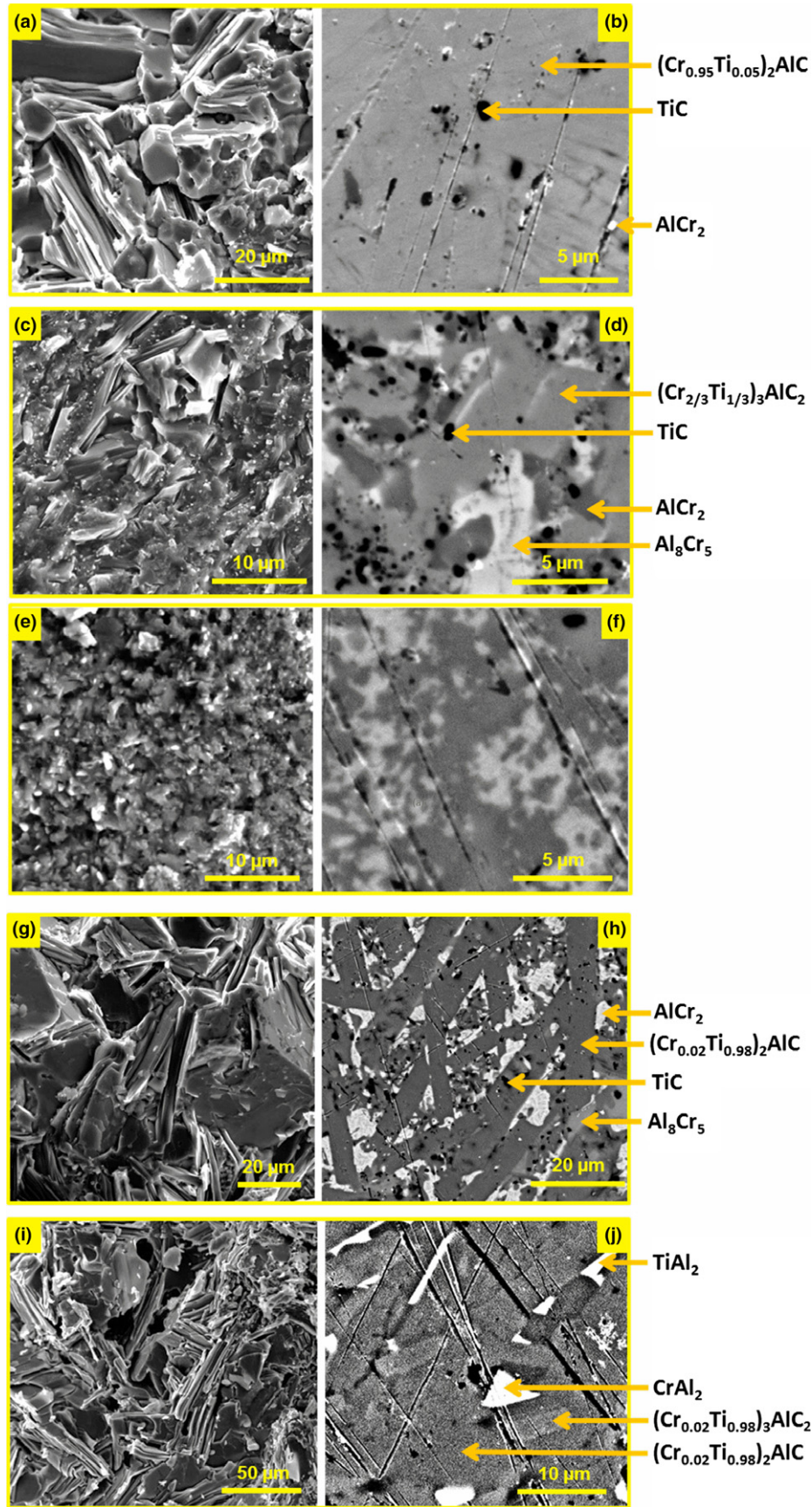


Fig. 2. SEM images (left column: SE imaging mode; right column: BSE imaging mode) of (a and b) *211-Cr95Ti5*, (c and d) *211-Cr75Ti25*, (e and f) *211-Cr50Ti50*, (g and h) *211-Cr25Ti75*, and (i and j) *211-Cr5Ti95*. Phase assignment was not possible for *211-Cr50Ti50* (e and f) as the grains are too small for proper EDX quantification.

Table I. Summary of Synthesis and Oxidation Tests Results

Acronym	Targeted compound	Observed phases (volume ratio)	MAX unit cell parameters (Å)	"Oxidation resistant" [†]
211-Cr95Ti5	(Cr _{0.95} Ti _{0.05}) ₂ AlC	(Cr _{0.95} Ti _{0.05}) ₂ AlC (>95%) + Al ₈₀ Cr ₂₀ (<5%) + TiC [§]	<i>a</i> = 2.867 (1) <i>c</i> = 12.863 (5)	Yes
211-Cr75Ti25	(Cr _{0.75} Ti _{0.25}) ₂ AlC	(Cr _{2/3} Ti _{1/3}) ₃ AlC ₂ (40%) + TiC (20%) + Al ₈ Cr ₅ (25%) + AlCr ₂ (15%)	<i>a</i> = 2.935 (1) <i>c</i> = 17.894 (7)	Yes
211-Cr50Ti50	(Cr _{0.5} Ti _{0.5}) ₂ AlC	(Cr _{0.95} Ti _{0.05}) ₂ AlC [‡] (21%) + TiC (42%) + Al ₈ Cr ₅ (22%) + AlCr ₂ (15%)	<i>a</i> = 2.867 (1) <i>c</i> = 12.83 (1)	Yes
211-Cr25Ti75	(Cr _{0.25} Ti _{0.75}) ₂ AlC	(Cr _{0.02} Ti _{0.98}) ₃ AlC ₂ (51%) + TiC (23%) + Al ₈ Cr ₅ (21%) + AlCr ₂ (5%)	<i>a</i> = 3.076 (2) <i>c</i> = 18.44 (2)	No
211-Cr5Ti95	(Cr _{0.05} Ti _{0.95}) ₂ AlC	(Cr _{0.02} Ti _{0.98}) ₂ AlC (50%) + (Cr _{0.02} Ti _{0.98}) ₃ AlC (45%) + TiAl ₂ (5%)	211: <i>a</i> = 3.0570 (6) <i>c</i> = 13.650 (3) 312: <i>a</i> = 3.0704 (6) <i>c</i> = 18.544 (5)	No
312-Cr5Ti95	(Cr _{0.05} Ti _{0.95}) ₃ AlC ₂	(Cr _{0.02} Ti _{0.98}) ₃ AlC ₂ (85%) + TiC (15%) + Al _x Cr _y [§]	<i>a</i> = 3.0744 (9) <i>c</i> = 18.567 (7)	No
312-Cr1/3Ti2/3	(Cr _{1/3} Ti _{2/3}) ₃ AlC ₂	TiC (65%) + Al ₈ Cr ₅ (28%) + AlCr ₂ (7%)	/	Yes
312-Cr50Ti50	(Cr _{0.5} Ti _{0.5}) ₃ AlC ₂	(Cr _{2/3} Ti _{1/3}) ₃ AlC ₂ (50%) + TiC (34%) + Al ₈ Cr ₅ (10%) + AlCr ₂ (6%)	<i>a</i> = 2.930 (3) <i>c</i> = 17.89 (2)	Yes
312-Cr2/3Ti1/3	(Cr _{2/3} Ti _{1/3}) ₃ AlC ₂	(Cr _{2/3} Ti _{1/3}) ₃ AlC ₂ (95%) + TiC (1%) + Al ₈ Cr ₅ (4%)	<i>a</i> = 2.9295 (9) <i>c</i> = 17.884 (7)	No

[†]"Yes" means the sample after the oxidation test has formed a protective and adherent scale. Conversely, "No" indicates the sample did not form a protective oxide scale and was fully or almost fully oxidized.

[‡]Cr/(Ti+Cr) ratio are of lesser precision for this phase due to other phases affecting EDX measurements, as suggested by higher scattering of measured values.

[§]Denotes when a phase is detected in a minor presence by SEM/EDX but not by XRD.

(2) Characterization of 312 Targeted Compounds

Synthesis of four 312 MAX phases was attempted: (Cr_{0.05}Ti_{0.95})₃AlC₂, (Cr_{1/3}Ti_{2/3})₃AlC₂, (Cr_{0.5}Ti_{0.5})₃AlC₂ and (Cr_{2/3}Ti_{1/3})₃AlC₂. The samples were denoted by 312-Cr5Ti95, 312-Cr1/3Ti2/3, 312-Cr50Ti50, and 312-Cr2/3Ti1/3, respectively. As for the previous series of compounds, SPS sintering had very minor or even no noticeable effects on the collected X-ray diffractograms.

XRD (Fig. 3) reveals that 312-Cr5Ti95 appears to have predominantly formed a 312 MAX phase. The lattice parameters obtained by refinement (Table I) fall in the range of values reported for Ti₃AlC₂.^{36–42,55,56} Comparison with simulated patterns of the α and β (Cr,Ti)₃AlC₂ polymorphs indicated without any ambiguity the α form was obtained, as always reported for Ti₃AlC₂.^{36,57} The only secondary phase detected by XRD is ~15 vol% of TiC. This is, however, in contradiction with SEM/BSE observations as less TiC was seen, while some grains of AlCr₂ were also found [Fig. 4(b)]. EDX characterization indicates the lamellar grains to have a (Al)/(Cr+Ti+Al) ratio of 23% \pm 3% and a Cr/(Cr+Ti) ratio

of 2% \pm 1% hence confirming a 312 MAX phase is formed but with less Cr than expected.

According to XRD analysis (Fig. 3) and as confirmed by SEM [Figs. 4(c) and (d)], the 312-Cr1/3Ti2/3 sample does not contain any MAX phase. The phases detected instead are TiC mostly and Al₈Cr₅ and AlCr₂.

The 312-Cr50Ti50 and 312-Cr2/3Ti1/3 compositions contain the (Cr_{2/3}Ti_{1/3})₃AlC₂ MAX phase in its α polymorph. This is verified by comparing the XRD lines (Fig. 3) with those reported by Liu et al.,^{32,33} by SEM imaging [lamellar structures, Figs. 4(e) and (g)] and by EDX point analysis of the lamellar grains: the Cr/(Cr+Ti) ratios are 66% \pm 1% and 65% \pm 3%, respectively, for 312-Cr50Ti50 and 312-Cr2/3Ti1/3, whereas the (Al)/(Cr+Ti+Al) ratios are 26% \pm 3% and 24% \pm 4%, as expected for (Cr_{2/3}Ti_{1/3})₃AlC₂. The 312-Cr2/3Ti1/3 synthesis led to almost fully pure targeted (Cr_{2/3}Ti_{1/3})₃AlC₂ with traces of TiC and Al₈Cr₅ (main XRD peaks barely detected). On the other hand 312-Cr50Ti50 unsurprisingly contains TiC as a main phase, accommodating excess titanium, but also Al–Cr alloys [Figs. 3 and 4(e) and (f)]. The lattice parameters of the (Cr_{2/3}Ti_{1/3})₃AlC₂ phases of 312-Cr50Ti50 and 312-Cr2/3Ti1/3 were close to each other (Table I) as well as with the values given by Liu et al.^{32,33}

The results presented in this section thus confirmed the existence and relative facility to produce the remarkable (Cr_{2/3}Ti_{1/3})₃AlC₂ phase obtained almost pure without optimizing any synthesis parameter (thermal cycles, reactant stoichiometry, etc.). More importantly, the ordering of Cr and Ti on the respective 4*f* and 2*a* Wyckoff sites apparently offers an enhanced stability which drives (Cr_{2/3}Ti_{1/3})₃AlC₂ formation although the required stoichiometry is inappropriate (i.e., when Cr and C are in excess in 211-Cr75Ti25 or when Ti is in excess compared to Cr in 312-Cr50Ti50). It seems clear that Cr₃AlC₂ and more generally Cr-based MAX phases with *n* \geq 2 are not stable due to Cr not being suited to be on the 2*a* Wyckoff site. Why Ti and Cr cannot share the 4*f* positions in the range 1/3 \leq Cr/(Cr+Ti) < 2/3 as observed for (Cr_{0.5}V_{0.5})₃AlC₂^{34,58} remains for the moment unexplained. However, the successful fabrication of (Cr_{0.05}Ti_{0.95})₃AlC₂ proved that a disordered solid solution remains achievable but only for low Cr contents since the 312-Cr1/3Ti2/3 sample does not produce any MAX phase.

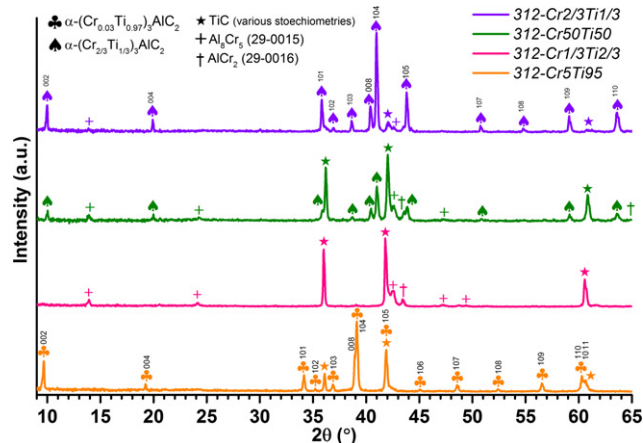


Fig. 3. X-ray diffractograms of 312 samples. Determination of crystalline phases was made using ICDD database and matched datashet numbers are indicated in parentheses.

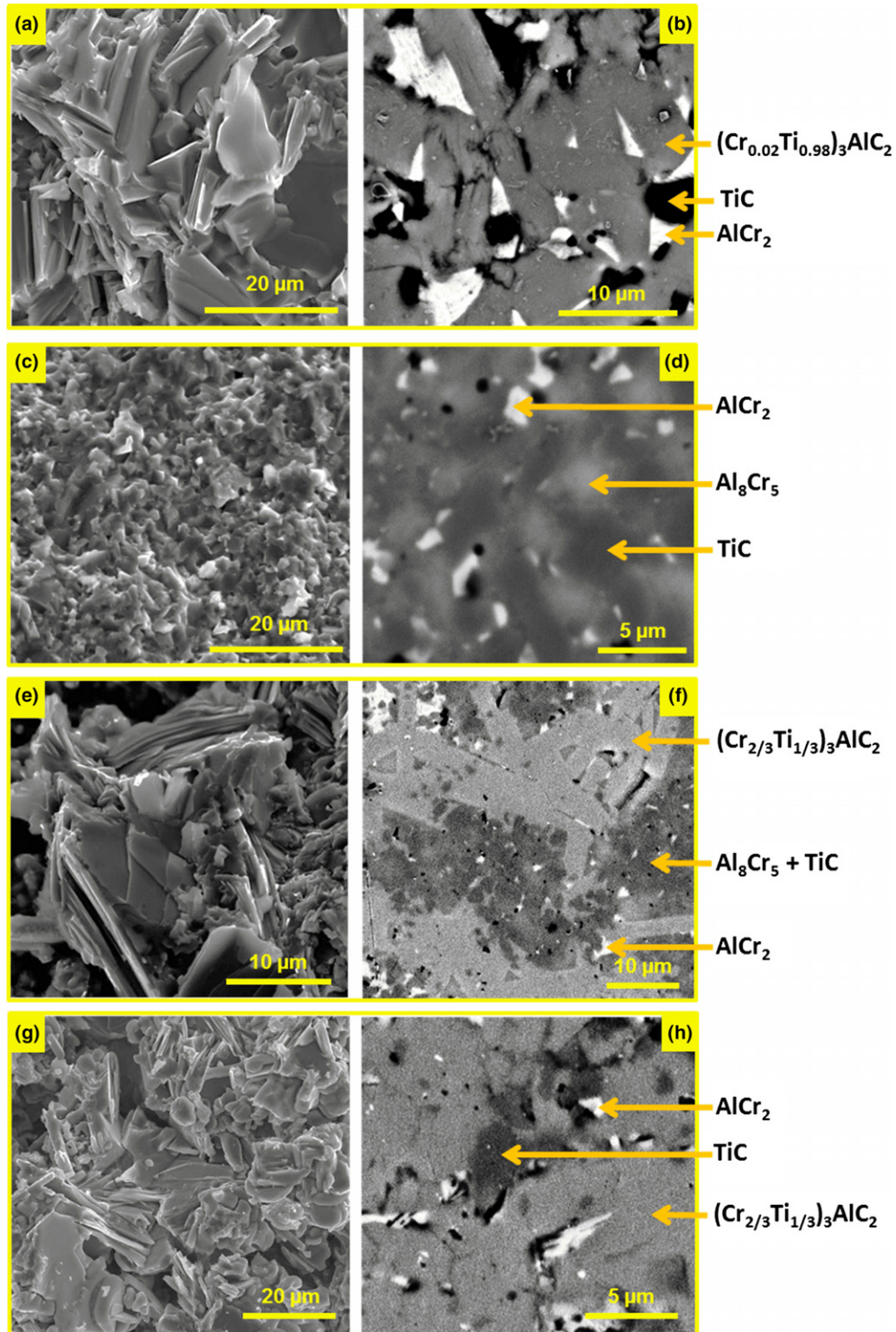


Fig. 4. SEM images (left column: SE imaging mode; right column: BSE imaging mode) of (a and b) *312-Cr5Ti95*, (c and d) *312-Cr1/3Ti2/3*, (e and f) *312-Cr50Ti50*, and (g and h) *312-Cr2/3Ti1/3*. Images (b) and (h) area were selected to highlight the different minor phases found and are far from being representative of the overall observed phase ratios.

The phases obtained for each sample are summarized in Table I.

(3) 1400°C Oxidation Tests

Oxidation tests in air at 1400°C for 12 h were performed for all sintered samples. Very different oxidation behaviors were noted and the samples can thereby be categorized in two groups: those that are experimentally resistant to oxidation and those which are not (Table I). In other words, some samples showed the ability to develop and maintain a

protective ~20 μm alumina scale (Fig. 5), while such a feature was not observed in other samples, leading to complete or almost complete oxidation of the material.

In Fig. 5(a), *211-Cr95Ti5* appears to have formed an adherent alumina layer surmounted by nonadherent TiO₂ and Al₂TiO₅ grains over up to 15 μm. Below the alumina layer the subsurface is found by EDX to be enriched to a depth of ~40 μm by chromium carbide phases (CrC_x), presumably Cr₃C₇. This carbide is often found at the subsurface of oxidized Cr₂AlC (and of (Cr_{0.95}Ti_{0.05})₂AlC²¹) as a by-product of the reaction between Cr₂AlC and O₂.^{1,59} The oxidized

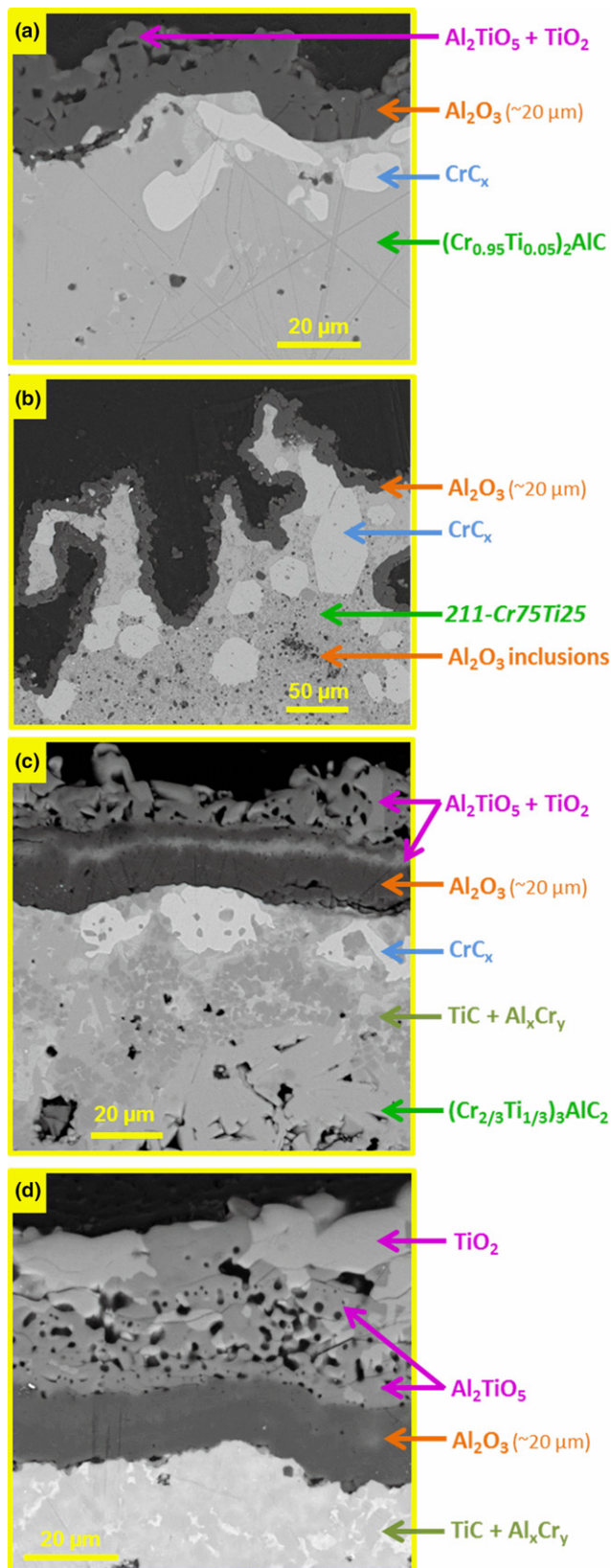


Fig. 5. Cross-sectional SEM images (BSE mode) after oxidation testing at 1400°C of (a) *211-Cr95Ti5*, (b) *211-Cr75Ti25*, (c) *312-Cr50Ti50*, and (d) *312-Cr1/3Ti2/3*. Indicated phases were determined from several EDX point analyses.

surface of *211-Cr75Ti25* [Fig. 5(b)] is very tortuous. Very few TiO_2 and Al_2TiO_5 grains are found on top of the protective Al_2O_3 scale. As for *211-Cr95Ti5* an enrichment of the subsurface by CrC_x is evidenced. Contrary to the other given

examples, a lot of 1–10 μm size Al_2O_3 inclusions are found in *211-Cr75Ti25* and these are found with a decreasing concentration up to few hundred microns deep in the coupon. *211-Cr50Ti50* cross section after the oxidation test (not shown) is very similar to *211-Cr75Ti25* with the one difference being it contains far less CrC_x domains. The oxide surface of *312-Cr50Ti50* [Fig. 5(c)] and *312-Cr1/3Ti2/3* [Fig. 5(d)] presents some similarities: in both cases the flat Al_2O_3 scale is surmounted by a highly porous and cracked 15 to 60 μm layer of $\text{TiO}_2 + \text{Al}_2\text{TiO}_5$. The subsurface of the two samples consist of TiC , Al_8Cr_5 , and AlCr_2 with some CrC_x domains found in *312-Cr50Ti50* only, probably due to the comparatively higher Cr content. The subsurface of *312-Cr50Ti50* is depleted in $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ and the latter is only found from $\sim 40 \mu\text{m}$ below the alumina layer [Fig. 5(c)]. From the SEM observations, it is suggested the oxidation mechanisms of the 5 “oxidation resistant” samples probably differ from each other.

At first sight, it is difficult to establish a relationship between the MAX phase composition and the oxidation resistance. A first interesting point is that among the failed samples, all but *312-Cr2/3Ti1/3* contain $(\text{Cr}_{0.02}\text{Ti}_{0.98})_3\text{AlC}_2$. In agreement with published oxidation kinetics values for Ti_2AlC , Cr_2AlC , and Ti_3AlC_2 ,¹ the latter thus offers less oxidation resistance which may explain the failure of these samples. Another interesting point concerns the MAX phase $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ which is found as the main component in *312-Cr2/3Ti1/3*, *312-Cr50Ti50*, and *211-Cr75Ti25*. Indeed, while *312-Cr50Ti50* and *211-Cr75Ti25* [Figs. 5(b) and (c)] show similar good oxidation behavior at 1400°C, *312-Cr2/3Ti1/3* is completely oxidized. It is then obvious that the MAX phase composition alone is, at least for this example, not decisive in determining oxidation resistance. What differentiates the three produced samples is the nature and relative quantities of secondary phases (Table I): *312-Cr50Ti50* and *211-Cr75Ti25* both contains notable amounts of TiC , which is highly suspected to lower MAX phases materials performance against HT oxidation,^{1,10,60} but they also contains several vol% of Al–Cr alloys. Searching the keywords “oxidation” and “ AlCr_2 ” or “ Al_8Cr_5 ” in the open literature, two publications relating the improvement of high-temperature oxidation resistance by these Al–Cr alloy phases were found.^{61,62} The most relevant is the work done by Lin et al.⁶¹ who synthesized a Cr–Al–C composite containing $\sim 40 \text{ wt}\%$ of Cr_2AlC , $\sim 14 \text{ wt}\%$ of Cr_7C_3 , $\sim 40 \text{ wt}\%$ of AlCr_2 , and $\sim 6 \text{ wt}\%$ of Al_8Cr_5 and studied its oxidation and hot-corrosion resistance (up to 1200°C in air). They observed the formation and the retention, even after cyclic testing, of a protective alumina layer and obtained oxidation kinetics similar to those of Cr_2AlC alone under the same conditions. They thus concluded that “the presence of AlCr_2 and Al_8Cr_5 could act as reservoir phases of Cr and Al and contribute to the protective scale formation by supplying Al and Cr”.

Based on the above observations and literature investigations, it is suggested Al–Cr alloys may improve the oxidation resistance of MAX phases. The reason why remains unclear at the current stage of this research and will need further investigations, however, it is likely the Al–Cr phases somehow enhance/favor the formation and stabilization of the all-important Al_2O_3 scale and simultaneously preclude the disruptive action of TiO_2 to be expressed. The Al–Cr alloys presumably contain some Ti and/or C, modifying their thermophysical properties, however, it is worth noting AlCr_2 and Al_8Cr_5 melting points are below the testing temperature (respectively around 910°C and 1320°C^{38,63}), which indicates liquid phases may play a role.

IV. Conclusions

Synthesis of nine $(\text{Cr,Ti})_2\text{AlC}$ and $(\text{Cr,Ti})_3\text{AlC}_2$ MAX phases was attempted by pressureless reaction followed by densification by SPS. From XRD and SEM/EDX characterizations,

mutual solubility of Ti₂AlC and Cr₂AlC appeared limited to a few atomic percent substitution, leading to the formation of several MAX + TiC + Al_xCr_y composites. Similarly Cr incorporation in Ti₃AlC₂ is low but possible as demonstrated by the first report of (Cr_{0.02}Ti_{0.98})₃AlC₂ synthesis. However, we confirm the existence and remarkable stability of (Cr_{2/3}Ti_{1/3})₃AlC₂ which tends to form even when the starting reactants are out of stoichiometric range.

A coupon of each sample was further tested against oxidation at 1400°C in air for 12 h. Five of the nine samples were found to self-protect against oxidation by forming a passivating ~20 μm thick Al₂O₃ layer, whereas the four others were totally oxidized. The results of this oxidation test, along with literature investigation, suggests (Cr_{2/3}Ti_{1/3})₃AlC₂ and (Cr_{0.02}Ti_{0.98})₃AlC₂ (and Ti₃AlC₂¹) are not oxidation resistant in the test conditions, contrary to (Cr_{0.95}Ti_{0.05})₂AlC (and Cr₂AlC and Ti₂AlC¹). However, the presence of Al-Cr phases is strongly thought to render the tested composite materials resilient in the test conditions as demonstrated by the formation of a dense, adherent and thus passivating and protective Al₂O₃ outer layer. This protection was even achieved when TiC_x is concomitantly present in large amounts (Table I), despite that this phase is known to disrupt the formation and stabilization of a protective Al₂O₃ layer. Recalling the industrial application motivating this work, composite materials consisting of a MAX phase or possibly a simple carbide associated with AlCr₂ and/or Al₈Cr₅ promoting the all-important alumina scale formation shall be considered for high-temperature Zr clad protection. The use of such composites, however, still needs to be evaluated in respect to the ageing behavior in nuclear reactor operating conditions (irradiation, 350°C pressurized water contact, etc.). Also numerous investigations (other testing temperatures and duration, notably) will be required to try to understand the mechanisms governing the high-temperature oxidation response of these Cr-Ti-Al-C composites.

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References

- ¹M. W. Barsoum, *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides*. Wiley-VCH, Weinheim, Germany, 2013.
- ²M. W. Barsoum and T. El-Raghy, "Synthesis and Characterization of a Remarkable Ceramic: Ti₃SiC₂," *J. Am. Ceram. Soc.*, **79** [7] 1953-6 (1996).
- ³M. W. Barsoum, B. G. Yaroshchuck, and S. Tyagi, "Fabrication and Characterization of M₂SnC (M = Ti, Zr, Hf and Nb)," *Ser. Mater.*, **37** [1] 1583-91 (1997).
- ⁴M. W. Barsoum, D. Brodtkin, and T. El-Raghy, "Layered Machinable Ceramics for High Temperature Applications," *Ser. Met. Mater.*, **36** [5] 535-41 (1997).
- ⁵D. J. Tallman, B. Anasori, and M. W. Barsoum, "A Critical Review of the Oxidation of Ti₂AlC, Ti₃AlC₂ and Cr₂AlC in Air," *Mater. Res. Lett.*, **1** [3] 115-25 (2013).
- ⁶J. W. Byeon, et al., "Microstructure and Residual Stress of Alumina Scale Formed on Ti₂AlC at High Temperature in Air," *Oxid. Met.*, **68** [12] 97-111 (2007).
- ⁷S. Basu, N. Obando, A. Gowdy, I. Karaman, and M. Radovic, "Long-Term Oxidation of Ti₂AlC in Air and Water Vapor at 1000-1300°C Temperature Range," *J. Electrochem. Soc.*, **159** [2] C90-6 (2012).
- ⁸Z. J. Lin, M. S. Li, J. Y. Wang, and Y. C. Zhou, "High-Temperature Oxidation and Hot Corrosion of Cr₂AlC," *Acta Mater.*, **55** [18] 6182-91 (2007).
- ⁹M. W. Barsoum, N. Tzenov, A. Procopio, and T. El-Raghy, "Oxidation of Ti_{n+1}AlX_n Where n = 1-3 and X is C, N, Part II: Experimental Results," *J. Electrochem. Soc.*, **148** [8] C551-62 (2001).
- ¹⁰X. H. Wang and Y. C. Zhou, "High Temperature Oxidation Behavior of Ti₂AlC in Air," *Oxid. Met.*, **59** [3-4] 303-20 (2003).
- ¹¹X. H. Wang and Y. C. Zhou, "Layered Machinable and Electrically Conductive Ti₂AlC and Ti₃AlC₂ Ceramics: A Review," *J. Mater. Sci. Technol.*, **26** [5] 385-416 (2010).

- ¹²B. Cui, D. D. Jayaseelan, and W. E. Lee, "Microstructural Evolution During High-Temperature Oxidation of Ti₂AlC Ceramics," *Acta Mater.*, **59** [10] 4116-25 (2011).
- ¹³H. J. Yang, Y. T. Pei, J. C. Rao, and J. T. M. De Hosson, "Self-Healing Performance of Ti₂AlC Ceramic," *J. Mater. Chem.*, **22**, 8304-13 (2012).
- ¹⁴X. Qian, X. D. He, Y. B. Li, Y. Sun, H. Li, and D. L. Xu, "Cyclic Oxidation of Ti₃AlC₂ at 1000-1300°C in Air," *Corros. Sci.*, **53** [1] 290-5 (2011).
- ¹⁵R. L. Coble and W. D. Kingery, "Effect of Porosity on Physical Properties of Sintered Alumina," *J. Am. Ceram. Soc.*, **39** [1] 377-85 (1956).
- ¹⁶M. W. Barsoum, M. Ali, and T. El-Raghy, "Processing and Characterization of Ti₂AlC, Ti₂AlN, and Ti₂AlC_{0.5}N_{0.5}," *Metall. Mater. Trans. A*, **31** [7] 1857-65 (2000).
- ¹⁷M. Sundberg, G. Malmqvist, A. Magnuson, and T. El-Raghy, "Alumina Forming High Temperature Silicides and Carbides," *Ceram. Int.*, **30** [7] 1899-904 (2004).
- ¹⁸D. B. Lee, T. D. Nguyen, and S. W. Park, "Long-Time Oxidation of Cr₂AlC Between 700 and 1,000°C in Air," *Oxid. Met.*, **77** [5-6] 275-87 (2012).
- ¹⁹D. B. Lee, T. D. Nguyen, J. H. Han, and S. W. Park, "Oxidation of Cr₂AlC at 1300°C in Air," *Corros. Sci.*, **49** [10] 3926-34 (2007).
- ²⁰S. Li, X. Chen, Y. Zhou, and G. Song, "Influence of Grain Size on High Temperature Oxidation Behavior of Cr₂AlC Ceramics," *Ceram. Int.*, **39** [3] 2715-21 (2012).
- ²¹D. B. Lee, T. D. Nguyen, and S. W. Park, "High Temperature Oxidation of a Nanolayer Laminated (Cr_{0.95}Ti_{0.05})₂AlC Compound in Air," *J. Nanosci. Nanotech.*, **10** [1] 319-24 (2010).
- ²²D. B. Lee and T. D. Nguyen, "Cyclic Oxidation of Cr₂AlC Between 1000 and 1300°C in Air," *J. Alloys. Compd.*, **464** [1-2] 434-9 (2008).
- ²³T. H. Scabarozzi, et al., "Thermal Expansion of Select MAX Phases Measured by High Temperature X-ray Diffraction and Dilatometry," *J. Appl. Phys.*, **105**, 013543, 8pp (2009).
- ²⁴T. Cabioch, P. Eklund, V. Mauchamp, M. Jaouen, and M. W. Barsoum, "Tailoring of the Thermal Expansion of Cr₂(Al_xGe_{1-x})C Phases," *J. Eur. Ceram. Soc.*, **33** [4] 897-904 (2013).
- ²⁵S. Bragg-Sitton, "Development of Advanced Accident Tolerant Fuels for Commercial LWRs," *Nucl. News*, 83-91 (2014).
- ²⁶E. N. Hoffman, D. W. Winson, R. L. Sindelar, D. J. Tallman, G. Kohse, and M. W. Barsoum, "MAX Phase Carbides and Nitrides: Properties for Future Nuclear Power Plant In-Core Applications and Neutron Transmutation Analysis," *Nucl. Eng. Des.*, **244**, 17-24 (2012).
- ²⁷V. F. Sears, "Neutron Scattering Lengths and Cross Sections," *Neutron News*, **3** [3] 26-37 (1992).
- ²⁸J. C. Schuster, H. Nowotny, and C. Vaccaro, "The Ternary Systems: Cr-Al-C, V-Al-C, and Ti-Al-C and the Behavior of H-Phases (M₂AlC)," *J. Solid State Chem.*, **32** [2] 213-9 (1980).
- ²⁹C. S. Kim, S. I. Hwang, J. S. Ha, S. M. Kang, and D. S. Cheong, "Synthesis of a Cr₂AlC-Ti₂AlC Ternary Carbide," *J. Ceram. Process Res.*, **11** [1] 82-6 (2010).
- ³⁰D. B. Lee, "Microstructural Analysis of Ti-Added Cr₂AlC Compounds After Air-Oxidation," *Surf. Interface Anal.*, **44** [11-12] 1453-5 (2012).
- ³¹G. B. Ying, et al., "Kinetics and Numerical Simulation of Self-Propagating High-Temperature Synthesis in Ti-Cr-Al-C Systems," *Rare Met.*, **33** [5] 527-33 (2014).
- ³²Z. Liu, L. Zheng, L. Sun, Y. Gian, J. Wang, and M. Li, "(Cr_{2/3}Ti_{1/3})₃AlC₂ and (Cr_{5/8}Ti_{3/8})₄AlC₃: New MAX-Phase Compounds in Ti-Cr-Al-C System," *J. Am. Ceram. Soc.*, **97** [1] 67-9 (2014).
- ³³Z. Liu, et al., "Crystal Structure and Formation Mechanism of (Cr_{2/3}Ti_{1/3})₃AlC₂ MAX Phase," *Acta Mater.*, **73**, 186-93 (2014).
- ³⁴E. N. Caspi, P. Chartier, F. Porcher, F. Damay, and T. Cabioch, "Ordering of (Cr,V) Layers in Nanolamellar (Cr_{0.5}V_{0.5})_{n+1}AlC_n Compounds," *Mater. Res. Lett.*, **3** [2] 100-6 (2015).
- ³⁵B. Anasori, J. Halim, J. Lu, C. A. Voigt, L. Hultman, and M. W. Barsoum, "Mo₂TiAlC₂: A New Ordered Layered Ternary Carbide," *Ser. Mater.*, **101**, 5-7 (2015).
- ³⁶N. V. Tzenov and M. W. Barsoum, "Synthesis and Characterization of Ti₃AlC₂," *J. Am. Ceram. Soc.*, **83** [4] 825-32 (2000).
- ³⁷B. B. Panigrahi, M.-C. Chu, Y.-I. Kim, S.-J. Cho, and J. J. Gracio, "Reaction Synthesis and Pressureless Sintering of Cr₂AlC Powder," *J. Am. Ceram. Soc.*, **93** [6] 1530-3 (2010).
- ³⁸L.-O. Xiao, S.-B. Li, G. Song, and W. G. Sloof, "Synthesis and Thermal Stability of Cr₂AlC," *J. Eur. Ceram. Soc.*, **31** [8] 1497-502 (2011).
- ³⁹V. Gauthier-Brunet, T. Cabioch, P. Chartier, M. Jaouen, and S. Dubois, "Reaction Synthesis of Layered Ternary Ti₂AlC Ceramic," *J. Eur. Ceram. Soc.*, **29** [1] 187-94 (2009).
- ⁴⁰E. H. Kisi, E. Wu, J. S. Zobel, J. S. Forrester, and D. P. Riley, "Inter-Conversion of M_{n+1}AX_n Phases in the Ti-Al-C System," *J. Am. Ceram. Soc.*, **90** [6] 1912-6 (2007).
- ⁴¹M. A. Pietzka and J. C. Schuster, "Summary of Constitutional Data on the Al-C-Ti System," *J. Phase Equilib.*, **15** [4] 392-400 (1994).
- ⁴²G. P. Bei, V. Gauthier-Brunet, C. Tromas, and S. Dubois, "Synthesis, Characterization, and Intrinsic Hardness of Layered Nanolaminate Ti₃AlC₂ and Ti₃Al_{0.8}Sn_{0.2}C₂ Solid Solution," *J. Am. Ceram. Soc.*, **95** [1] 102-7 (2012).
- ⁴³T. Roinsel and J. Rodriguez-Carvajal, "WinPLOTR: A Windows Tool for Powder Diffraction Pattern Analysis," *Mater. Sci. Forum*, **378** [1] 118-23 (2011).
- ⁴⁴J. M. Schneider, Z. M. Sun, R. Mertens, F. Uestel, and R. Ahuja, "Ab Initio Calculations and Experimental Determination of the Structure of Cr₂AlC," *Solid State Commun.*, **130** [7] 445-9 (2004).
- ⁴⁵Z. Lin, Y. Zhou, M. Li, and J. Wang, "Solid-Liquid Reaction Synthesis of Bulk Cr₂AlC," *Z. Metallkd.*, **96** [3] 291-6 (2005).

- ⁴⁶W. B. Tian, P. L. Wang, G. J. Zhang, Y. M. Kan, and Y. X. Li, "Mechanical Properties of Cr₂AlC Ceramic," *J. Am. Ceram. Soc.*, **90** [5] 1663–6 (2007).
- ⁴⁷J. Wang, J. Wang, A. Li, J. Li, and Y. Zhou, "Theoretical Study on the Mechanism of Anisotropic Thermal Properties of Ti₂AlC and Cr₂AlC," *J. Am. Ceram. Soc.*, **97** [4] 1202–8 (2014).
- ⁴⁸Z. Sun, R. Ahuja, S. Li, and J. M. Schneider, "Structure and Bulk Modulus of M₂AlC (M= Ti, V, and Cr)," *Appl. Phys. Lett.*, **83** [5] 899–901 (2003).
- ⁴⁹G. Hug, M. Jaouen, and M. W. Barsoum, "X-ray Absorption Spectroscopy, EELS, and Full-Potential Augmented Plane Wave Study of the Electronic Structure of Ti₂AlC, Ti₂AlN, Nb₂AlC, and (Ti_{0.5}Nb_{0.5})₂AlC," *Phys. Rev. B*, **71**, 024105, 12pp (2005).
- ⁵⁰B. Manoun, F. X. Zhang, S. K. Saxena, T. El-Raghy, and M. W. Barsoum, "X-Ray High Pressure Study of Ti₂AlN and Ti₂AlC," *J. Phys. Chem. Solids*, **67**, 2091–4 (2006).
- ⁵¹W. Yu, V. Gauthier-Brunet, T. Cabioch, and S. Dubois, "Synthesis and Microstructural Characterization of Substoichiometric Ti₂Al(C_xN_y) Solid Solutions and Related Ti₂AlC_x and Ti₂AlN End-Members," *J. Am. Ceram. Soc.*, **97** [7] 2308–13 (2014).
- ⁵²W. B. Zhou, B. C. Mei, J. Q. Zhu, and X. L. Hong, "Rapid Synthesis of Ti₂AlC by Spark Plasma Sintering Technique," *Mater. Lett.*, **59** [1] 131–4 (2005).
- ⁵³J. P. Guha and D. Kolar, "The Systems TiC–Cr and ZrC–Cr," *J. Less Com. Met.*, **31** [3] 337–43 (1973).
- ⁵⁴V. Raghavan, "Al–Cr–Ti (Aluminium–Chromium–Titanium)," *J. Phase Equilib. Diffus.*, **31** [6] 548–9 (2005).
- ⁵⁵H. Zhang, X. Wu, K. G. Nickel, J. Chen, and V. Presser, "High-Pressure Powder X-ray Diffraction Experiments and *Ab Initio* Calculation of Ti₃AlC₂," *J. Appl. Phys.*, **106**, 013519, 5pp (2009).
- ⁵⁶Y. C. Zhou, J. X. Chen, and J. Y. Wang, "Mechanism for the Strengthening of Ti₃AlC₂ by Incorporation of Si to Form Ti₃Al_{1-x}Si_xC₂ Solid Solutions," *Acta Mater.*, **54** [5] 1317–22 (2006).
- ⁵⁷A. Zhou, C. A. Wang, and Y. Huang, "Synthesis and Mechanical Properties of Ti₃AlC₂ by Spark Plasma Sintering," *J. Mater. Sci.*, **38** [14] 3111–5 (2003).
- ⁵⁸Y. Zhou, F. Meng, and J. Zhang, "New MAX Phase Compounds in the V–Cr–Al–C System," *J. Am. Ceram. Soc.*, **91** [4] 1357–60 (2008).
- ⁵⁹W. Tian, P. Wang, Y. Kan, and G. Zhang, "Oxidation Behavior of Cr₂AlC Ceramics at 1,100 and 1,250°C," *J. Mater. Sci.*, **43** [8] 2785–91 (2008).
- ⁶⁰M. W. Barsoum, L. H. Ho-Duc, M. Radovic, and T. El-Raghy, "Long Time Oxidation Study of Ti₃SiC₂, Ti₃SiC₂/SiC, and Ti₃SiC₂/TiC Composites in Air," *J. Electrochem. Soc.*, **150** [4] B166–75 (2003).
- ⁶¹Z. J. Lin, M. S. Li, J. Y. Wang, and Y. C. Zhou, "Microstructure and High-Temperature Corrosion Behavior of a Cr–Al–C Composite," *J. Am. Ceram. Soc.*, **90** [12] 3930–7 (2007).
- ⁶²M. Ueda, D. Susukida, S. Konda, and T. Ohtsuka, "Improvement of Resistance of TiAl Alloy Against High Temperature Oxidation by Electroplating in AlCl₃–NaCl–KCl–CrCl₂ Molten Salt," *Surf. Coat. Technol.*, **176** [2] 202–8 (2004).
- ⁶³H. Okamoto, "Al–Cr (Aluminum–Chromium)," *J. Phase Equilib. Diff.*, **29** [1] 112–3 (2008). □