1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

On the Interactions of Ti_2AlC , Ti_3AlC_2 , Ti_3SiC_2 and Cr_2AlC with Silicon Carbide and Pyrolytic Carbon at 1300 °C

G. W. Bentzel,^{*} M. Ghidui, B. Anasori, and M. W. Barsoum,

Department of Materials Science & Engineering, Drexel University, Philadelphia, PA 19104, USA

This work was supported by the Department of Energy's Office of Nuclear Energy University Program under Grant CFP-11-3231.

^{*}Corresponding author: Email – gwb29@drexel.edu, Phone – +1-717-676-5521

Keywords: MAX Phase, Diffusion, Nuclear Application, Characterization

Abstract:

Herein we report on the reactivity between silicon carbide, SiC, and pyrolytic carbon, PG, with the MAX phases, Ti_2AlC , Ti_3AlC_2 , Ti_3SiC_2 and Cr_2AlC . Diffusion couples were assembled and heated to 1300 °C under a load corresponding to a uniaxial stress of ~ 30 MPa for four, ten, and thirty hours in a vacuum hot press, at a vacuum level of less than 1 Pa. The couples were then examined using optical and scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and orientation image microscopy. Based on the totality of the results – after 30 h at 1300 °C – it is concluded that neither Ti_3SiC_2 nor Cr_2AlC appear to react with SiC. The former also appears not to react with PG. When heated in the vacuum of the hot press, both Ti_2AlC and Ti_3AlC_2 dissociated to form TiC surface layers that were $\approx 15\text{-}20$ μm thick. After reaction of Ti_2AlC with SiC and PG, the TiC layer was only ≈ 10 μm thick, indirectly confirming that the dissociation of these phases in vacuum was due to the Al evaporation from the surfaces. The $\text{Ti}_3\text{AlC}_2/\text{SiC}$ and $\text{Ti}_3\text{AlC}_2/\text{PG}$ diffusion couples resulted in TiC layers that were ≈ 50 μm and ≈ 100 μm thick, respectively. The $\text{Cr}_2\text{AlC}/\text{PG}$ diffusion couple resulted in the formation of ≈ 10 μm interfacial layer comprised of Cr_3C_2 and Cr_7C_3 at the interface between the two materials.

Introduction:

The $M_{n+1}AX_n$ phases are ternary, thermodynamically stable nanolayered carbides and nitrides, where M is an early transition metal, A is a group A element, mostly from groups 13 and 14, and X is C and/or N.¹ They are hexagonally structured, with the $P6_3/mmc$ space group.¹ There are over 70 known MAX phases, which are further categorized by their n value as “211s” for M_2AX ($n = 1$), “312s” for M_3AX_2 ($n = 2$) and “413s” for M_4AX_3 ($n = 3$) etc.² These materials combine some of the more attractive properties of ceramics and metals. As with most metals, they have high electric and thermal conductivities,³⁻⁵ are easily machinable,⁶ and possess exceptional thermal shock resistance and damage tolerance.^{3,5,7} Some, such as Ti_2AlC and Ti_3SiC_2 , are lightweight, stiff and creep,⁸⁻¹² oxidation,¹³⁻¹⁶ and fatigue¹⁷ resistant.

Recently the MAX phases have been proposed for use in the nuclear industry.^{18,19} However, before the MAX phases can even be considered for use in such applications, and to better understand where they would be most judiciously used, much needs to be better understood and quantified. A systematic research effort into the chemical stability/reactivity of the MAX phases is required to determine their feasibility in nuclear applications such as high temperature structural components or diffusion barrier coatings for nuclear fuels. In fuel applications, such as coatings, the candidate materials must be evaluated for chemical interactions from the outside of the fuel pellet toward the fuel, as well as, the fuel and fission product inside the fuel pellet toward the coolant. Furthermore, joining the MAX phases to materials currently being used and/or proposed for the next generation nuclear reactor such as the nuclear fuel, graphite, SiC and other materials needs to be quantified.

Currently, there is limited research in the open literature on the chemical stability of the MAX phases vis-à-vis materials for nuclear systems. Certain MAX phases have been tested for corrosion in select coolant environments. For example, it has been shown that Ti_3SiC_2 has superb corrosion resistance to molten Pb and Pb-Bi alloys.^{20,21} The diffusion between Zircaloy-4 and the MAX phases Ti_3SiC_2 and Ti_2AlC in the 1100-1300 °C range has also been explored.²² These results show the A-group element diffusing out of the MAX phase and forming intermetallics with the Zr-4, with the penetration depth of the Si in Ti_3SiC_2 being roughly an order of magnitude less than that of the Al from the Ti_2AlC .

1 Silicon carbide, SiC, and pyrolytic graphite, PG, are used as diffusion barrier
2 layers in the TRISO fuel design.²³ A MAX phase layer may prove to be useful in
3 extending the lifetime of TRISO fuel pellets. They could be used either as an additional
4 layer that maintains thermal diffusion efficiency, or as a substitute to the current SiC
5 layer. Furthermore, because Ti_2AlC and Ti_3AlC_2 form thin alumina protective layers
6 when heated in air they have been shown to have excellent oxidation resistance at
7 temperature up of 1400 °C, even under severe cyclic heating conditions.²⁴ The same
8 compounds are also stable in high vacuum, to temperature up to 1400 °C.²⁵ At 1000 and
9 1100 °C, Cr_2AlC also forms a thin alumina layer, but with a thin Cr_7C_3 underlayer.²⁶ At
10 1200 and 1300 °C, an outer $(Al_{1-x},Cr_x)_2O_3$ mixed oxide layer, an intermediate Cr_2O_3
11 oxide layer, an inner Al_2O_3 oxide layer, and a Cr_7C_3 underlayer form. At these
12 temperatures, spallation occurs, limiting oxidation resistance of Cr_2AlC to no higher
13 than 1100 °C, or even 1000 °C.²⁷

14 Herein, we focus on the interactions of four MAX phases, Ti_2AlC , Ti_3AlC_2 ,
15 Ti_3SiC_2 , and Cr_2AlC , with PG and SiC at 1300 °C, for times up to 30 h.

16 Experimental Procedure:

17 The Ti_2AlC samples were prepared by loading pre-reacted Ti_2AlC powders (-
18 325 mesh, Kanthal, Hallstahammar, Sweden) in a graphite die that was, in turn, placed
19 in a graphite heated in a hot press HP, for 4 h at 1300 °C under a load corresponding to
20 a stress of ≈ 30 MPa. . The Ti_3AlC_2 sample was prepared by hot pressing, pre-reacted
21 Ti_2AlC (-325 mesh, Kanthal, Hallstahammar, Sweden) and TiC (2 μm powder, 99.5%,
22 Alfa Aesar, Ward Hill, MA) powders in a 1:1 ratio to make 3:1:2 stoichiometry of
23 $Ti:Al:C$. Powders were ball milled for 24 h, placed in a graphite die, and heated in the
24 HP at a rate of 500 °C/h to 1400 °C. The sample was held for 4 h under a load
25 corresponding to a pressure of ~ 40 MPa, before furnace cooling.

26 The polycrystalline Ti_3SiC_2 samples were prepared by loading pre-reacted
27 Ti_3SiC_2 powders (-325 mesh, Kanthal, Hallstahammar, Sweden) in a graphite die, that
28 was in turn placed in a HP, heated to 1500 °C, and held at that temperature for 4 h,
29 under a load corresponding to a stress of ≈ 30 MPa, before furnace cooling.

30 The Cr_2AlC samples were prepared by ball milling a 2:1:1 stoichiometric
31 mixture of Cr (-325 mesh, 99%, Alfa Aesar, Ward Hill, MA), Al (-325 mesh, 99.5%,
32 Alfa Aesar, Ward Hill, MA), and graphite (-325 mesh, 99%, Alfa Aesar, Ward Hill,
33

1 MA) powders for 24 h. This mixture was then poured into a graphite mold and HPed at
2 1400 °C for 4 h, under a load corresponding to a pressure of ~ 40 MPa. In all cases the
3 vacuum level was less than 1 Pa.
4

5 The various MAX samples were cut using a diamond saw into ~ 0.3 x 1.5 x 1.5
6 cm³ parallelepipeds. The slices were then sandwiched between PG (Substrate nucleated,
7 ultra-pure, GraphiteStore, Buffalo Grove, IL) on one side and SiC (CVD SiC, 99%,
8 Rohm and Haas Chemical LLC, Marlborough, MA) on the other, placed in the HP, and
9 heated to 1300 °C under a load corresponding to a pressure of ~20 MPa for 4 h, 10 h, or
10 30 h, at a vacuum level of less than 1 Pa. The size of the PG and SiC slices were
11 roughly 1.5 x 1.5 cm² in cross-section with thicknesses of 0.3 cm and 0.5 cm,
12 respectively.
13
14
15
16
17
18
19

20 Since some of the MAX phases can dissociate in and/or react with the C-rich
21 environments of a graphite heated HP,²⁸ a sample of each composition was heated in the
22 HP at 1300 °C for 30 h under a vacuum of 1 Pa.
23
24
25

26 Upon cooling, the samples were cross-sectioned and mounted in epoxy, ground
27 and polished for examination in a scanning electron microscope (SEM), (FEI Zeiss
28 Supra 50VP, Jena, Germany) equipped with an energy-dispersive X-ray spectroscope
29 (EDS), (Oxford INCA X-Sight 7573, Abingdon, England). Electron backscatter
30 diffraction (EBSD) was carried out in a second SEM (FEI XL30, Hillsboro, OR) using
31 EDAX's (AMETEK, Berwyn, PA) orientation image microscopy (OIM) hardware.
32
33
34
35
36

37 An optical microscope, OM, was used to image the etched surfaces of each
38 sample. The etchant used for the Ti₂AlC, Ti₃AlC₂, and the Ti₃SiC₂ samples was a 1:1:1
39 part solution of hydrofluoric acid (48%, Sigma Aldrich, St. Louis, MO), nitric acid
40 (68%, Alfa Aesar, Ward Hill, MA), and water. A drop of etchant was placed on the
41 surface of each samples and rinsed after 2-3 s. For the Cr₂AlC sample, a drop of
42 hydrofluoric acid (48%, Sigma Aldrich, St. Louis, MO) was placed on the surface of the
43 sample and rinsed after ~2 min.
44
45
46
47
48

49 X-ray diffraction (XRD) patterns of the surface of the Cr₂AlC samples in contact
50 with SiC, as well as the surface in contact with PG, were obtained, using a
51 diffractometer (Rigaku SmartLab, Tokyo, Japan) with a 5 mm or 2 mm slit, depending
52 on sample size. The scans were conducted over the range of 5° to 70° 2θ, with a step
53 size of 0.02° and a dwell time of 0.5 s per step. Rietveld refinements of the XRD
54
55
56
57
58
59
60
61
62
63
64
65

patterns were conducted using *FullProf*.²⁹ Refined parameters were: 6 background parameters, lattice parameters of all phases, and their phase fractions.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Figure 1: Rietveld refinements of powder XRD patterns of, a) Ti_2AlC , b) Ti_3AlC_2 , c) Ti_3SiC_2 , and, d) Cr_2AlC . Observed pattern is shown in black crosses, Rietveld generated pattern in red and the difference between the two in blue.

Ti_2AlC

Figure 2a shows the OM image of the polished and etched surface of the Ti_2AlC control sample after heating to 1300 °C in the vacuum of the HP. Since this particular Ti_2AlC sample did not color when etched (Fig. 2a) it is difficult to determine from the OM micrograph whether a TiC layer forms on its surface or not. To solve this problem we obtained a TiC EBSD map of the surface layer (inset in Fig. 2a) from which it is unequivocal that a 10-15 μm TiC layer forms on the surface. Based on the OM micrograph, one can conclude that the Ti_2AlC sample was fully dense and that the grain size was between 20-30 μm .

Figure 2: Microstructure Ti_2AlC after heating to 30 h at 1300 °C in vacuum, a) OM micrographs of cross-sectional polished and etched surface. Inset is an EBSD map of TiC confirming the formation of a 10 μm thick TiC layer. In contact with SiC for 30 h at 1300 °C, b) OM micrographs of etched surface; c) backscatter electrons SEM micrograph. In contact with PG for 30 h at 1300 °C, d) OM micrographs of etched surface; e) backscatter electrons SEM micrograph, EBSD maps of, f) Ti_2AlC and g) TiC in f. The interface is near the right edge.

Figures 2b and c show, respectively, the OM micrograph of the etched surface and the respective SEM micrograph of the Ti_2AlC interface after interaction with SiC at 1300 °C for 30 h. It is obvious that a thin, less than 10 μm thick TiC layer, is present. Interestingly, compared to the control sample (Fig. 2a), it is reasonable to conclude that less Al is lost from the Ti_2AlC surface when the latter was in contact with SiC, than when heated in the vacuum of the HP.

In the case of Ti_2AlC after interaction with PG at 1300 °C for 30 h (Fig. 2d and e), the OM image of the etched surface (Fig. 2d) shows a thin TiC layer of $\approx 10 \mu\text{m}$ forming at the surface. The evidence for the presence of this layer is best seen by comparing the EBSD images shown in Figs. 2f and g.

Ti_3AlC_2

Figure 3a shows the OM image of the polished and etched surface of the Ti_3AlC_2 control sample after heating to 1300 °C in the vacuum of the HP. Based on these results, it is clear that Ti_3AlC_2 forms a 15-20 μm thick, bright layer on the surface. It follows that both Ti_2AlC and Ti_3AlC_2 form a $\approx 15 \mu\text{m}$ thick TiC layers by the selective evaporation of Al from the basal planes.³¹ Based on the OM micrograph, one can also conclude that the Ti_3AlC_2 sample was fully dense and that the grain size was $\approx 100 \mu\text{m}$.

For Ti_3AlC_2 after interaction with SiC at 1300 °C for 30 h, the results (Figs. 3b and c), again clearly show the formation of a 30-40 μm thick TiC reaction layer (white layer in Fig. 3b) at the interface. Since this layer is 15-25 μm thicker than the one heated in vacuum (Fig. 3a), we conclude that more Al is lost near the interface when Ti_3AlC_2 is in contact with SiC, than when heated in the vacuum of the HP.

Figure 3: Microstructure Ti_3AlC_2 after heating to 30 h at 1300 °C in vacuum, a) OM micrographs of cross-sectional polished and etched surface. In contact with SiC for 30 h at 1300 °C, b) OM micrographs of etched surface; c) backscatter electrons SEM micrograph. In contact with PG for 30 h at 1300 °C, d) OM micrographs of etched surface; e) backscatter electrons SEM micrograph, EBSD maps of, f) Ti_3AlC_2 and g) TiC in f. The interface is near the right edge.

For the Ti_3AlC_2 phase after interaction with PG (Fig. 3d and e) at 1300 °C for 30 h, it is clear that a $\approx 100 \mu\text{m}$ thick TiC layer formed along the interface (Fig. 3d). Figure

3g confirms this reaction layer to be ~100 μm thick. Furthermore, EDS (not shown) and EBSD maps (Figs. 3g) unambiguously identify this phase to be TiC.

According to the Ti-Al-C ternary phase diagram, both Ti_2AlC and Ti_3AlC_2 should react with C to first form TiC and TiAl_3 , after which the latter should further react with the C to form Al_4C_3 and TiC. As noted above, the evidence for the presence of TiC is clear. However, no evidence was found for Al_4C_3 . Possible reasons for this state of affairs are several and include the dissolution of Al_4C_3 during polishing and or its dissociation and evaporation under the testing conditions. These comments notwithstanding, it is hereby acknowledged that more work needs to be carried out to understand why no evidence for this phase is found.

Ti₃SiC₂

The Ti_3SiC_2 (Fig. 4a) surface does not appear to be affected by heating to 1300 °C for 30 h in vacuum, at least at the magnifications shown in Fig. 4a. Ti_3SiC_2 has been reported to decompose, at temperatures of 1300 °C and higher in vacuum, into TiC_y , with $\text{Ti}_5\text{Si}_3\text{C}_x$ as an intermediate phase.³² However, in this work, this was not observed. Based on the OM micrograph, one can conclude that the Ti_3SiC_2 sample was fully dense and that the grain size was between 20-30 μm .

Based on Figs. 4b and c, it is reasonable to conclude that no reaction occurs between Ti_3SiC_2 and SiC, even after annealing at 1300 °C for 30 h. This result, however, is not too surprising, given that, according to the Ti-Si-C ternary phase diagram,³³ Ti_3SiC_2 should be in equilibrium with SiC.

Figure 4: Microstructure Ti_3SiC_2 after heating to 30 h at 1300 °C in vacuum, a) OM micrographs of cross-sectional polished and etched surface. In contact with SiC for 30 h at 1300 °C, b) OM micrographs of etched surface; c) backscatter electrons SEM micrograph. In contact with PG for 30 h at 1300 °C, d) OM micrographs of etched surface; e) backscatter electrons SEM micrograph, EBSD maps of, f) Ti_3SiC_2 and g) TiC in f. The interface is near the right edge.

Also according to the Ti-Si-C ternary phase diagram, carbon should react with Ti_3SiC_2 to form SiC and TiC. However, neither BS SEM micrographs (Fig. 4d), EDS,

EBSD (Figs. 4f and g), nor XRD of the Ti_3SiC_2 side of the interface (not shown) show any evidence for the formation of any reaction layers at the interface. The TiC particles found within the bulk form during the fabrication process.

Cr₂AlC

The Cr_2AlC (Fig. 5a) surface also does not appear to be affected by heating to 1300 °C for 30 h in vacuum. Cr_2AlC has been found to have excellent stability, in vacuum, up to 1450 °C.³⁴ At higher temperatures, decomposition occurs due to the sublimation of Cr and Al. Based on the OM micrograph (Fig. 5a), one can conclude that the Cr_2AlC sample was fully dense and that the grain size was between 20-30 μm .

Based on Figs. 5b and c, it is reasonable to conclude that no reaction occurs between Cr_2AlC and SiC, even after annealing at 1300 °C for 30 h. XRD results of the interface on the Cr_2AlC side (not shown) confirmed that no extra phases formed between the two materials.

Figure 5: Microstructure Cr_2AlC after heating to 30 h at 1300 °C in vacuum, a) OM micrographs of cross-sectional polished and etched surface. In contact with SiC for 30 h at 1300 °C, b) OM micrographs of etched surface; c) backscatter electrons SEM micrograph. In contact with PG for 30 h at 1300 °C, d) OM micrographs of etched surface; e) backscatter electrons SEM micrograph.

In the case of Cr_2AlC , after interaction with PG at 1300 °C for 30 h, and according to the OM and SEM micrographs, shown in Figs. 5d and e, respectively, there appears to be no evidence for a reaction. EBSD maps (not shown), however, show clear signs of Cr_7C_3 forming at the interface. To confirm the nature of the phases that form at the interface, XRD of the Cr_2AlC side of the diffusion couple was carried out. The results, shown in Fig. 6, unambiguously prove that not only does Cr_7C_3 form, but also Cr_3C_2 (Fig. 6b). According to the 1000 °C Cr-Al-C ternary phase diagram,³⁵ Cr_2AlC should react with C to form Cr_3C_2 and Al_4C_3 . Why Cr_7C_3 is present is unclear but suggests that possibly the phase diagram at 1300 °C is different than the 1000 °C one.

Why Al_4C_3 is not present is again not clear, but in this case since no water was used, its absence cannot be due to its dissolution. We thus conclude that this phase most probably dissociates into Al and C at higher temperatures and that the C then further reacts with MAX phase, as the Al, presumably, evaporates away.

Figure 6: XRD patterns of the surface of, a) unreacted Cr_2AlC and, b) Cr_2AlC after heating in contact with PG for 30 h at 1300 °C under a load corresponding to a stress of 30 MPa. Black squares represent peak positions of Cr_2AlC , blue circles those for Cr_7C_3 , and red triangles those for Cr_3C_2 .

In summary, it appears that neither Ti_2AlC , Ti_3SiC_2 nor Cr_2AlC react with SiC after being in contact with the latter for 30 h at 1300 °C. The situation for the Ti_3AlC_2 is more ambiguous, but it appears that the presence of SiC, for reasons that are not entirely clear, enhances its decomposition. No evidence for a reaction was found between Ti_3SiC_2 nor Ti_2AlC (above that in vacuum) with PG. In the case of Cr_2AlC , neither OM nor SEM micrographs show much evidence for a reaction. However, XRD results unambiguously showed that Cr_7C_3 and Cr_3C_2 formed at the interface with the PG. In the case of Ti_3AlC_2 , the TiC layer was about 100 μm thick. In all cases, the MAX and both the SiC and PG phases were separated by layer of epoxy used for mounting the samples, indicating that the bonding, after cooling to room temperature, between the

various MAX phases, with either SiC or PG, if present, was quite weak which allowed the epoxy to penetrate into the interface during sample preparation and mounting.

Summary and Conclusions:

Herein we report for the first time on the reactions or lack thereof, at 1300 °C and for times as long as 30 h under a load corresponding to a stress of about 30 MPa, between SiC and PG with Ti_2AlC , Ti_3AlC_2 , Ti_3SiC_2 and Cr_2AlC .

Neither Ti_3SiC_2 nor Cr_2AlC showed any evidence of a reaction with SiC. The 10 μm thick layer of TiC formed on Ti_2AlC was thinner than the corresponding layer formed when Ti_2AlC was heated in the vacuum of the hot press. Said otherwise, the presence of SiC must have slowed down the escape of the Al from the Ti_2AlC phase. The TiC layer that formed on Ti_3AlC_2 , on the other hand, was roughly double the ~15 μm thick layer that formed in the vacuum of the hot press.

No evidence for a reaction was found between Ti_3SiC_2 or Ti_2AlC (above that in vacuum) with PG. In the case of Cr_2AlC , neither OM or SEM micrographs show much evidence for a reaction. However, XRD unambiguously showed that Cr_7C_3 and Cr_3C_2 formed at the interface with the PG. In the case of Ti_3AlC_2 , the TiC layer was about 100 μm thick.

Acknowledgements:

This work was funded by the Department of Energy's Office of Nuclear Energy University Program (CFP-11-3231).

References

1. M. W. Barsoum, 'The $M_{N+1}AX_N$ phases: A new class of solids: Thermodynamically stable nanolaminates,' *Prog. Solid State Chem.*, **28**, 201-281 (2000).
2. C. Hu, H. Zhang, F. Li, Q. Huang, and Y. Bao, 'New phases' discovery in MAX family,' *Inter. J. Refract. Metals and Hard Mater.*, **36**, 300-312 (2013).
3. M. W. Barsoum and T. El-Raghy, 'Synthesis and Characterization of a Remarkable Ceramic: Ti_3SiC_2 ,' *J. Am. Ceram. Soc.*, **79** [7] 1953-1956 (1996).
4. M. W. Barsoum and T. El-Raghy, 'Progress report on Ti_3SiC_2 , Ti_3GeC_2 , and H-phases, M_2BX ,' *J. Mater. Synth. and Proc.*, **5**, 197-216 (1997).

5. T. El-Raghy, A. Zavaliangos, M. W. Barsoum, and S. R. Kalindindi, 'Damage Mechanism around Hardness Indentations in Ti_3SiC_2 ,' *J. Am. Ceram. Soc.*, **80** [2] 513-516 (1997).
6. M. W. Barsoum and T. El-Raghy, 'The MAX Phases: Unique New Carbide and Nitride Materials,' *Am. Sci.*, **89**, 336-345 (2001).
7. A. Ganguly, T. Zhen, and M. W. Barsoum, 'Synthesis and mechanical properties of Ti_3GeC_2 and $\text{Ti}_3(\text{Si}_x\text{Ge}_{1-x})\text{C}_2$ ($x=0.5, 0.75$) solid solutions,' *J. Alloys and Comp.*, **376**, 287-295 (2004).
8. D. J. Tallman, M. Naguib, B. Anasori, and M. W. Barsoum, 'Tensile creep of Ti_2AlC in air in the temperature range 1000-1150 °C,' *Scripta Mater.*, **66**, 805-808 (2012).
9. M. Radovic, M. W. Barsoum, T. El-Raghy, and S. Wiederhorn, 'Tensile creep of fine grained (3-5 μm) Ti_3SiC_2 in the 1000-1200 °C temperature range,' *Acta Mater.*, **49**, 4103-4112 (2001).
10. M. Radovic, M. W. Barsoum, T. El-Raghy, and S. M. Wiederhorn, 'Tensile creep of coarse-grained Ti_3SiC_2 in the 1000-1200 °C temperature range,' *J. of Alloys and Comp.*, **361**, 299-312 (2003).
11. T. Zhen, M. W. Barsoum, S. R. Kalidindi, M. Radovic, Z. M. Sun, and T. El-Raghy, 'Compressive creep fine and coarse-grained Ti_3SiC_2 in air in the 1100-1300 °C temperature range,' *Acta Mater.*, **53** [19] 4963-4973 (2005).
12. T. A. Prikhna, S. N. Dub, A. V. Starostina, M. V. Karpets, T. Cbiosh, and P. Chartier, 'Mechanical properties of materials based on MAX phases of the Ti-Al-C system,' *J. Superhard Mater.*, **34** [2] 102-109 (2012).
13. M. W. Barsoum, T. El-Raghy, and L. Ogbuji, 'Oxidation of Ti_3SiC_2 in Air,' *J. Electro. Soc.*, **144**, 2508-2516 (1997).
14. S. B. Li, X. D. Chen, Y. Zhou, and G. M. Song, 'Influence of grain size on high temperature oxidation behavior of Cr_2AlC ceramics,' *Ceram. Inter.*, **39** [3] 2715-2721 (2013).

15. X. H. Wang and Y. C. Zhou, 'Layered Machinable and Electrically Conductive Ti_2AlC and Ti_3AlC_2 Ceramics: a Review,' *J. Mater. Sci. & Tech.*, **26** [5] 385-416 (2010).
16. M. Sundberg, G. Malmqvist, A. Magnusson, and T. El-Raghy, 'Alumina forming high temperature silicides and carbides,' *Ceram. Inter.*, **30** [7] 1899-1904 (2004).
17. S. Li, G. Song, K. Kwakernaak, S. vand der Zwaag, and W. G. Sloof, 'Multiple crack healing of a Ti_2AlC ceramic,' *J. Euro. Ceram. Soc.*, **32** [8] 1813-1820 (2012).
18. M. K. Patel, D. J. Tallman, J. A. Valdez, J. Aguiar, O. Anderoglu, M. Tang, J. Griggs, E. Fu, Y. Wang, and M. W. Barsoum, 'Effect of helium irradiation on Ti_3AlC_2 at 500 °C,' *Scripta Materialia*, **77**, 1-4 (2014).
19. E. N. Hoffman, D. W. Vinson, 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,' *Nuc. Eng. And Design*, **244**, 17-24 (2012).
20. L. A. Barnes, N. L. Dietz Rago, and L. Leibowitz, 'Corrosion of ternary carbides by molten lead,' *J. Nucl. Mater.*, **373**, 424-428 (2008).
21. A. Heinzl, G. Muller, and A. Weisenburger, 'Compatibility of Ti_3SiC_2 with liquid Pb and PbBi containing oxygen,' *J. Nucl. Mater.*, **392**, 255-258 (2009).
22. D. J. Tallman, J. Yang, L. Pan, B. Anasori, and M. W. Barsoum, 'Reactivity of Zircaloy-4 with Ti_3SiC_2 and Ti_2AlC in the 1100-1300 °C temperature range,' *J. Nuc. Mat.*, **460**, 122-129 (2015).
23. T. Allen, J. Busby, M. Meyer, and D. Petti, 'Materials Challenges for Nuclear Systems,' *Materials Today*, **13**, 14 (2010).
24. M. Sundberg, G. Malmqvist, A. Magnusson, and T. El-Raghy, 'Alumina Forming High Temperature Silicides and Carbides,' *Ceramics International*, **30**, 1899-1904 (2004).
25. D. Tallman, B. Anasori, and M. W. Barsoum, 'A Critical Review of the Oxidation of Ti_2AlC , Ti_3AlC_2 and Cr_2AlC in Air,' *Mater. Res. Lett.*, **1**, 115-125 (2013).
26. D. B. Lee and T. D. Nguyen, 'Cyclic oxidation of Cr_2AlC between 1000 and 1300 °C in

- air,' *J. Alloys Compds.*, **464**, 434-439 (2008).
27. I. M. Low, W. K. Pang, S. J. Kennedy, and R. I Smith, 'High-temperature thermal stability of Ti_2AlN and Ti_4AlN_3 : A comparative diffraction study,' *J. Eur. Ceram. Soc.*, **31**, 159-166 (2011).
 28. T. El-Raghy and M. W. Barsoum, 'Diffusion kinetics of the carburization and silicidation of Ti_3SiC_2 ,' *J. Applied Phys.*, **83**, 112-119 (1998).
 29. Rodriguez-Carvajal J, 'Recent advances in magnetic structure determination by neutron powder diffraction,' *Physica B.*, 1993, **192**, 55-69.
 30. W.J.J Wakelkamp, F.J.V Loo, and R. Metselaar, 'Phase relations in the Ti-Si-C system,' *J. Eur. Ceram. Soc.*, **8**, 135 (1991).
 31. J. Frodelius, P. Eklund, M. Beckers, P. Persson, H. Höglberg, and L. Hultman, 'Sputter deposition from Ti_2AlC target: Process characterization and conditions for growth of Ti_2AlC ,' *Thin Solid Films*, 518, 1621-1626 (2010).
 32. J. Zeng, S. Ren, and J. Lu, 'Phase Evolution of Ti_3SiC_2 Annealing in Vacuum at Elevated Temperatures,' *Int. J. Appl. Ceram. Technol.*, **10**, 527-539 (2013).
 33. D. Bandyopadhyay, 'The Ti-Si-C System (Titanium-Silicon-Carbon),' *J. Phase Equilibria and Diff.*, **25**, 415-420 (2004).
 34. W.K. Pang, I.M. Low, B.H. O'Connor, A.J. Studer, V.K. Peterson, Z.M. Sun, and J.-P. Palmquist, 'Comparison of thermal stability in MAX 211 and 312 phases,' *J. of Phys.: Conf. Series*, **251**, 1-4 (2010).
 35. A. I. Gusev, 'Phase equilibria in M-X-X' and M-Al-X ternary systems (M = transition metal; X, X' = B, C, N, Si) and the crystal chemistry of ternary compounds,' *Russian Chemical Reviews*, **65**, 379-419 (1996).

Figure

Figure 1: Rietveld refinements of powder XRD patterns of, a) Ti_2AlC , b) Ti_3AlC_2 , c) Ti_3SiC_2 , and, d) Cr_2AlC . Observed pattern is shown in black crosses, Rietveld generated pattern in red and the difference between the two in blue.

Figure 2: Microstructure Ti_2AlC after heating to 30 h at 1300 °C in vacuum, a) OM micrographs of cross-sectional polished and etched surface. Inset is an EBSD map of TiC confirming the formation of a 10 μm thick TiC layer. In contact with SiC for 30 h at 1300 °C, b) OM micrographs of etched surface; c) backscatter electrons SEM micrograph. In contact with PG for 30 h at 1300 °C, d) OM micrographs of etched surface; e) backscatter electrons SEM micrograph, EBSD maps of, f) Ti_2AlC and g) TiC in f. The interface is near the right edge.

Figure 3: Microstructure Ti_3AlC_2 after heating to 30 h at 1300 °C in vacuum, a) OM micrographs of cross-sectional polished and etched surface. In contact with SiC for 30 h at 1300 °C, b) OM micrographs of etched surface; c) backscatter electrons SEM micrograph. In contact with PG for 30 h at 1300 °C, d) OM micrographs of etched surface; e) backscatter electrons SEM micrograph, EBSD maps of, f) Ti_3AlC_2 and g) TiC in f. The interface is near the right edge.

Figure 4: Microstructure Ti_3SiC_2 after heating to 30 h at 1300 °C in vacuum, a) OM micrographs of cross-sectional polished and etched surface. In contact with SiC for 30 h at 1300 °C, b) OM micrographs of etched surface; c) backscatter electrons SEM micrograph. In contact with PG for 30 h at 1300 °C, d) OM micrographs of etched surface; e) backscatter electrons SEM micrograph, EBSD maps of, f) Ti_3SiC_2 and g) TiC in f. The interface is near the right edge.

Figure 5: Microstructure Cr_2AlC after heating to 30 h at 1300 °C in vacuum, a) OM micrographs of cross-sectional polished and etched surface. In contact with SiC for 30 h at 1300 °C, b) OM micrographs of etched surface; c) backscatter electrons SEM micrograph. In contact with PG for 30 h at 1300 °C, d) OM micrographs of etched surface; e) backscatter electrons SEM micrograph.

Figure 6: XRD patterns of the surface of, a) unreacted Cr_2AlC and, b) Cr_2AlC after heating in contact with PG for 30 h at 1300 °C under a load corresponding to a stress of 30 MPa. Black squares represent peak positions of Cr_2AlC , blue circles those for Cr_7C_3 , and red triangles those for Cr_3C_2 .