Reactivity of Zircaloy-4 with Ti_3SiC_2 and Ti_2AlC in the 1100 to 1300 °C Temperature Range

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Abstract:

*Herein, we report on the interactions between zirconium, in the form of Zircaloy-4 (Zr-4) and the MAX phases, Ti_3SiC_2 and Ti_2AlC in the 1100-1300 °C range. In both cases, the A-group element, Al or Si, diffused out of the MAX phases and formed intermetallics with the Zr-4. Under comparable conditions, Si penetration into the Zr-4 was roughly an order of magnitude less than that of the Al from the Ti_2AlC . The **effective** diffusion coefficient of Si can be described by $D_{eff_Si}(\frac{m^2}{s}) = 7.4 \times 10^{-9} \exp(\frac{-170 \text{ kJ/mol}}{RT})$; that of Al by $D_{eff_Al}(\frac{m^2}{s}) = 9.2 \times 10^{-12} \exp(\frac{-38 \text{ kJ/mol}}{RT})$. At 38 kJ/mol, the activation energy for the Ti_2AlC /Zr-4 diffusion bonding process was significantly lower than **that of** the Ti_3SiC_2 /Zr-4 diffusion couples, at 170 kJ/mol.*

Keywords: Zircaloy-4; Ti_3SiC_2 ; Ti_2AlC ; Diffusion

1. Introduction

Zircaloy-4 (Zr-4) is widely used as fuel cladding in light water reactors (LWR), mainly due to its high strength, corrosion resistance and low neutron **interaction** cross section. However, its poor oxidation resistance can lead to its failure under loss of coolant conditions [1-3]. α -zirconium (α -Zr) maintains an HCP structure **to temperatures as high as 850 °C**. Above 950 °C, a phase change occurs resulting in FCC β -zirconium (β -Zr) [4]. LWRs nominally operate up to 400 °C, well within the α -Zr region for Zr-4 [5]. Loss-of-coolant accidents (LOCA), however, can lead to fuel rods experiencing temperatures in excess of 1200 °C, their rupture due to increased pressure, and exposure to the atmosphere with catastrophic consequences [4].

Another issue with Zr-4 cladding is its susceptibility to water corrosion, specifically hydrogen pickup and embrittlement [6]. Dissolved oxygen in the coolant water reacts with the metal surface, leading to the formation of a protective layer of ZrO_2 . Simultaneously, the hydrogen produced from the oxidation diffuses into the cladding, resulting in the generation of zirconium hydride, ZrH_2 , precipitates, which lead to hydrogen embrittlement, decreases in fracture toughness, and the acceleration of corrosion and irradiation swelling [6]. Mitigation of hydrogen pickup and cladding oxidation is thus vital for the longevity and accident tolerance of fuel rod assemblies for use in LWRs. As important, isolating the Zr-cladding during normal operating conditions could allow for higher burn-up and possibly higher operating temperatures. One solution to the corrosion problem, that could also increase the safety of a LWR in LOCA, is to hermetically seal them from their surroundings. We recently proposed that the MAX phases in general, and Ti_2AlC in particular, can be used to as a thin coating onto existing Zr-4 cladding [7].

The MAX phases are a class of layered, machinable, early transition metal ternary carbides and nitrides that possess an unusual combination of ceramic and metallic properties. These thermodynamically stable nanolaminates are thermally and electrically conductive and machinable [8]. Some, like Ti_3SiC_2 and Ti_2AlC , are also light-weight, possess high fracture toughness values, and are oxidation and thermal shock resistant [8-9]. These compounds have also been shown to be creep resistant at high temperatures, and go through a brittle-to-plastic transition at $\sim 1000^\circ\text{C}$ [10-12].

Recent work has shown that Ti_3SiC_2 and Ti_3AlC_2 are resilient to heavy ion irradiation, resisting amorphization up to 25 dpa [13-22]. Neutron activation calculations, confirmed by neutron irradiation transmutation analysis, have shown that specific activities of Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC compare well with SiC after 10-60 years decay [23]. Very recently, we showed that Ti_2AlC and Ti_3SiC_2 maintain phase stability and crystallinity after neutron irradiation up to 0.1 dpa [24]. These MAX phases thus show promise for use in nuclear applications. Before such applications can even be considered, however, their interactions with Zr-4 need to be understood and quantified. Before doing so, it is instructive to review what is known of the interactions between Zr-4 and various solids at elevated temperatures.

Diffusion bonding of stainless steels to Zr-4 has been widely studied [25-27]. In 1978, Shaaban *et al.* [25] investigated Zr-4 diffusion bonding with 304 stainless steel. Successful bonding was achieved at 950°C and 1000°C . The resulting microstructure, however, was rich in hard ZrCr_2 intermetallics, leading to a brittle diffusion bond. More recently, Taouinet *et al.* [27] characterized the solid state diffusion interface between Zr-4 and 304L stainless steel, showing the formation of 3 distinct layers: A zone of $\alpha\text{-FeCr}$ solid solution, an area rich in the

intermetallic compound $\text{Zr}(\text{Fe},\text{Cr})_2$, and a third zone, composed of α -Zr and the intermetallic $\text{Zr}_2(\text{Fe}_{1-x}\text{Ni}_x)$. The Cr-rich layer, adjacent to the steel side, acted as a diffusion barrier.

To enhance bonding, and mitigate the formation of brittle intermetallics, some have tried to use intermediate layers [28-30]. For example, Ahmad *et al.* [28] investigated the Zr-4/304L diffusion zone morphology in the presence of a tantalum, Ta, intermediate layer at 1150 °C. Akhter *et al.* showed that local melting and the formation of dendritic structures occurred between Zr-4 and stainless steel when a titanium, Ti, intermediate layer was used above 1050 °C [29-30]. They reported the formation of the eutectic phases $\text{Zr}(\text{Fe},\text{Ni})_2$ - TaCr_2 and $\text{Ta}(\text{Cr},\text{Fe})_2$ - Ta_2Ni_3 on the stainless steel side in the Ta foil and in stainless steel, and $\text{Ta}(\text{Cr},\text{Fe})_2$ - $\text{Zr}(\text{Fe},\text{Cr})_2$ - Zr_3Ta_2 and $\text{Ta}(\text{Fe},\text{Cr})_2$ - $\text{Liq.}-\beta\text{-Zr}$ and TaCr_2 - $\text{Liq.}-\beta\text{-Zr}$ in Zr-4. Here again the Cr-rich zone, adjacent to the stainless steel acted as a diffusion barrier [28].

More germane to this work are the several studies that have investigated the interdiffusion of silicon, Si or Al into Zr. Kidson *et al.* [31] showed that bonding Al to Zr for hydrogen mitigation led to the formation of a singular ZrAl_3 bonding layer, even though 10 intermetallics are known to form between the two elements. Yue *et al.* [32] explored the diffusion profile of Al that was laser clad onto a Zr substrate. The resulting diffusion layer was composed of a series of phases: $(\text{Zr}) \rightarrow \text{Zr} + \text{AlZr}_2 + \text{AlZr}_3 \rightarrow \text{Al}_4\text{Zr}_5 + \text{Al}_3\text{Zr}_2 \rightarrow \text{Al}_3\text{Zr}_2 + \text{AlZr}_2 \rightarrow \text{Al}_2\text{Zr} \rightarrow \text{Al}_2\text{Zr} + \text{Al}_3\text{Zr}$. Laik *et al.* [33] reported the activation energy of diffusion, Q_d , of -220 ± 3.33 kJ/mol and D_0 of $5.57^{+2.6}_{-1.8} \times 10^{-6}$ m²/s for the temperature dependence of Al impurity diffusion into β -Zr, in the 1203 - 1323 K temperature range.

The Si-Zr system is known to have seven intermetallics: ZrSi_2 , ZrSi , Zr_5Si_4 , Zr_3Si_2 , Zr_5Si_3 , Zr_2Si , and Zr_3Si [34]. Bertolino *et al.* [35] reported the formation of a double layered diffusion

layer between Zr and Si in the 1173–1623 K temperature range. After long enough annealing times, ZrSi_2 became the major phase on the Si-rich side. The thickness of that layer increased parabolically with time and its thickness was temperature dependent. On the Zr side, a thin ZrSi layer, whose thickness only depended on temperature, formed.

Diffusion bonding of the MAX phases has also been the subject of several papers. Gao and Miyamoto investigated joining Ti_3SiC_2 with a Ti-6Al-4V alloy, resulting in the formation of $\text{Ti}_5\text{Si}_3\text{C}_x$ and TiC interfacial phases. Above 1350 °C, a liquid-state was presumed to have formed [36]. Yin *et al.* [37] successfully joined Ti_3SiC_2 to itself by using an Al-interlayer. Ganguly *et al.* [38] reported the interdiffusion coefficients for the A-group element (Si, Ge) to be > 300 times greater than the M-elements (Ti and Nb). Dong *et al.* [39] successfully bonded SiC parts to themselves, in the 1200 to 1600 °C temperature range, using an intermediate Ti_3SiC_2 layer. The strength of the bond was good because of the chemical bonds formed and the plasticity and thermal stress relaxation of the Ti_3SiC_2 layer. Above 1000 °C, Gu *et al.* [40] bonded Ti_3SiC_2 to itself using Ti-metal layer that resulted in the formation of TiC_x , Ti_5Si_3 and TiSi_2 within the diffusion zone.

The purpose of this paper is to report, for the first time, on the diffusion bonding of Zr-4 to Ti_3SiC_2 and Ti_2AlC in the 1100-1300 °C range.

2. Experimental Details

Details of the synthesis of the MAX phases are discussed elsewhere [41]. In brief, samples of Ti_3SiC_2 and Ti_2AlC , henceforth denoted as TSC and TAC, respectively, were prepared by pouring pre-reacted powders (Kanthal, Hallstahammar, Sweden) into graphite dies that, in turn, were loaded into a vacuum hot press and hot pressed (HPed) for 4 h under a uniaxial

load corresponding to a stress of ~ 40 MPa and a vacuum of 10^{-1} Pa at temperatures of 1500 and 1300 °C, for TSC and TAC respectively.

Samples were sectioned via high-speed diamond saw into nominally 12x12x3 mm³ plates. Zr-4 samples (Westinghouse, Cranberry Township, PA, USA) were machined from a 10 mm diameter rod stock into 3 mm thick discs via electro-discharge machining. The top and bottom faces of all samples were then ground parallel with silicon carbide grit paper and polished to a final surface finish with a 1 μ m diamond suspension.

Diffusion couples were formed with the Zr foil typically sandwiched between two different MAX phases (see inset in Fig. 1a). Alumina plates were placed in between the MAX phases and the graphite punch that was used to transfer an applied load corresponding to a stress of ~ 2.5 MPa. The entire assembly was then placed into 36 mm diameter graphite dies. The diffusion tests were performed in a vacuum hot press for 1, 2, 10 and 30 h at temperatures of 1100, 1200, and 1300 °C, under a vacuum of 10^{-1} Pa, before furnace cooling.

The resulting diffusion couples were cross sectioned with a high speed diamond saw, mounted, and polished with a final surface preparation of 1 μ m diamond suspension polish. An etchant with a volume ratio HF(50%) : HNO₃(70%) : 5H₂O was used to expose the microstructures of select samples.

Diffusion profiles were obtained using a scanning electron microscope, SEM, (Carl Zeiss Supra 50VP, Germany) equipped with an energy-dispersive X-ray spectroscope, EDX, (Oxford Inca X-Sight, Oxfordshire, UK). EDX line scans were used to generate elemental concentration profiles across the various interfaces. Point scans were also used to identify the chemical composition of the various intermetallic diffusion layers.

Calculation of diffusion coefficients from the diffusion profiles was problematic since in most cases more than one distinct intermetallic layers formed, each presumably with its own diffusion coefficient. To partially solve this problem and partially quantify the kinetics, the total diffusion distance, x , defined here as the total thickness of all intermetallic phases was measured as a function of time, t , in seconds. If the overall process is diffusion controlled and

$$x (m) = \sqrt{2D_A t} \quad (1)$$

then plots of x vs. $t^{1/2}$ should yield straight lines with slopes that are proportional to the effective chemical diffusion coefficient, D_A , of the solute species into Zr-4. The temperature dependence of D_A then follows the Arrhenius equation

$$D_A = D_o e^{\left(\frac{-Q_A}{RT}\right)} \quad (2)$$

where D_o , Q_A , R and T are the pre-exponential term, activation energy for diffusion, universal gas constant, and temperature in Kelvin, respectively.

3. Results and Discussion

Like most MAX phases' interactions with other solids, herein the A-group element, Al or Si, diffused out of the MAX phases' basal planes and formed intermetallics with the surrounding Zr-4 matrices. In the Al case, was also found deeper in the Zr matrices. SEM micrographs of the diffusion zones between Zr-4, on the one hand, and TSC and TAC, on the other, reveal the formation of multiple intermetallic layers (Figs. 1 and 2). Diffusion profiles across the interfaces reveal that the diffusion of Ti and Zr was quite limited (Figs. 3 and 4). In the following sections, first the interactions of Zr-4 with TSC and TAC are discussed separately. In the final section, the diffusivities and behavior of the two systems are compared and contrasted.

Figure 1. Typical backscattered electron SEM micrographs of $\text{Ti}_3\text{SiC}_2/\text{Zr-4}$ diffusion couples annealed at a) 1100 °C (etched), b) 1200 °C, and c) 1300 °C (etched) for 30 h. The layers A, B, C, D, E, F, and G correspond to the phases $(\text{Zr,Ti})\text{Si}$, ZrSi_2 , ZrSi , Zr_3Si_2 , Zr_2Si , Zr_3Si , and $\beta\text{-Zr+Si}$, respectively. In each case, a thin layer of porosity is observed at the interface. The predominant layer is composed of ZrSi . Occasional cracks, denoted by white arrows, are observed parallel to the interface. Inset of a) shows a schematic of the diffusion couple loading assembly that was in turn placed in the hot press. A layer of epoxy is seen in a) where the diffusion couple fractured during sample mounting.

Figure 2. Typical backscattered electron SEM micrographs of $\text{Ti}_2\text{AlC}/\text{Zr-4}$ diffusion couples annealed at a) 1100 °C (etched), b) 1200 °C (etched), and c) 1300 °C for 30 h. The layers A, B, C, D, and E correspond to the phases Zr_2Al_3 , Zr_5Al_4 , Zr_3Al_2 , Zr_2Al , and Zr_3Al , respectively. In all cases, a layer of epoxy is seen where the diffusion couple fractured during sample mounting. Zr_3Al precipitates are observed along the β -Zr grain boundaries beyond the intermetallic layers. At 1300 °C, no single layer dominates. Significant cracking of the intermetallic layers is observed parallel and perpendicular to the original interface.

Figure 3. Typical composition profiles of constituent elements determined by EDX line scans normal to the $\text{Ti}_3\text{SiC}_2/\text{Zr-4}$ interfaces obtained after annealing at, a) 1100 °C, b) 1200 °C, and c) 1300 °C for 30 h reveal the formation of several intermetallic layers with distinct compositions. A depletion of Si is seen on the Ti_3SiC_2 side at 1100 °C (a), though not at higher temperatures. There is a slight counter diffusion of Ti and Zr, though Si is the dominant diffusing species. At 1300 °C, a layer of ZrSi_2 is observed.

Figure 4. Typical composition profiles of constituent elements determined by EDX line scans normal to the $\text{Ti}_2\text{AlC}/\text{Zr-4}$ interfaces obtained after annealing at, a) 1100 °C, b) 1200 °C, and c) 1300 °C for 30 h reveal the formation of several intermetallic layers with distinct compositions. Each condition tested resulted in similar phase compositions, with layer thickness increasing with temperature. During annealing at the temperatures tested, the Al dissolves into solution with

β -Zr beyond the intermetallic layers on the Zr-4 side. Upon cooling, Al segregation at the grain boundaries likely resulted in the precipitation of Zr_3Al structures, seen in Fig. 2.

3.1 Ti_3SiC_2

Typical SEM micrographs of TSC/Zr diffusion couples are shown in Fig. 1. Table 1 summarizes the phases formed as a function of time and temperature. Based on the totality of our results the following conclusions can be reached:

- i) The main intermetallic phase that forms is ZrSi (Fig. 1; Table 1). At 1100 °C after less than 10 h, the ZrSi does not contain Ti (Table 1). At higher temperatures, in areas adjacent to the TSC phase, some Ti dissolves in the ZrSi phase (Table 1).
- ii) $ZrSi_3$ forms under all conditions save for 30h at 1300 °C. For the most part, its thickness is less than that of ZrSi.
- iii) After annealing for 30 h at 1100 °C (Fig. 1a), $t > 1$ h at 1200 °C (Fig. 5b and 1b) and at all times at 1300 °C (Table 1), the Zr_2Si phase is present.
- iv) Not surprisingly, at the highest temperatures, the number of phases and their intermixing increase substantially (Fig. 1 and Table 1).

As noted above, Bertolino *et al.* [35] reported that two phases - $ZrSi_2$ and ZrSi - formed when Si and Zr diffusion couples were annealed. The thickness of the $ZrSi_2$ layer increased parabolically with time and its thickness was temperature dependent. On the Zr side, a thinner ZrSi layer, whose thickness only depended on temperature, formed. A crude estimate of the overall diffusion coefficient through the reaction layer at 900 °C yields of value of $4 \times 10^{-13} \text{ m}^2/\text{s}$. Unfortunately this value cannot be compared with our result (see below) of $3.1 \times 10^{-15} \text{ m}^2/\text{s}$ calculated at 1100 °C, since they were obtained at different temperatures.

Table 1: Summary of phase compositions and their thicknesses, in μm , across the $\text{Ti}_3\text{SiC}_2/\text{Zr-4}$ diffusion couples - starting with Ti_3SiC_2 - as a function of time and temperature. The last column lists the total thickness of the reaction layer and is the one plotted in Fig. 6.

Time (h)	(ZrTi)Si	ZrSi ₂	ZrSi	Zr ₃ Si ₂	Zr ₂ Si	Zr ₃ Si	$\beta\text{-Zr} + \text{Si}$	Total Diffusion Thickness
1100 °C								
1	-	-	6.2(1)		-	1.4(1)	-	7.6(2)
2	-	-	6.4(1)		-	1.4(1)	-	7.8(1)
10	0.4(1)	-	15.4(1)	1.2(1)	-	1.8(1)	-	18.7(2)
30	0.9(1)	-	22.7(1)	-	2.2(1)	2.2(1)	-	27.9(3)
1200 °C								
1	0.5(1)	-	6.4(1)	-	-	1.3(1)	-	8.2(1)
2	0.8(1)	-	7.2(1)	1.3(1)	0.7(1)	5.4(1) 8% Ti	2.13(7)	17.5(2)
10	-	-	15.7(3) 3% Ti		4.0(1) 1% Ti	3.1(1)	-	23.0(4)
30	1.3(1)	-	24.7(5) 5% Ti		1.6(1)	7.4(2)	1.9(3)	36.9(7)
1300 °C								
2	0.84(4)	-	20.7(2)	-	2.9(1)	1.0(1)	-	25.5(2)
10	3.1(2)	8.1(3) 5% Ti	5.0(4) 5% Ti	-	10.4(3)	7.6(2)	2.0(1)	36.2(8)
30	4.7(1)	15.4(3) 5% Ti	40.3(6)	2.0(2)	10.0(2)	-	2.6(1)	75.2(8)

‡ Uncertainty = (1)

Based on these results it is reasonable to conclude that the overall reaction or diffusion path between TSC and Zr-4 is:

Phases shown in bold formed under most conditions. A layer close to the TSC side with a phase corresponding to a solid solution (Zr, Ti)Si was observed after 10 h at 1100 °C and at both 1200 and 1300 °C. Only at 1300 °C after 10 h and 30 h was a ZrSi₂ phase observed. A thin layer of a composition corresponding to Zr₃Si₂ was sporadically observed after annealing for 10 h at 1100 °C, 2 h at 1200 °C, and 30 h at 1300 °C. The Zr₂Si phase was more common after longer times

and higher temperatures, appearing after 30 h at 1100 °C and at times longer than 1 h at both 1200 and 1300 °C.

No precipitates were seen to form beyond the intermetallic layers. Slight porosity at the interface was observed at 1100 °C after annealing for 30 h and at 1200 °C and above (Figs. 1a-c). Occasional cracks were observed parallel to the interface (Figs. 1c and 5a). In general, the TSC diffusion couples resulted in firmly bonded interfaces that were able to withstand the clamping forces applied during sectioning, polishing, etc.

Figure 5. Typical backscattered electron SEM micrographs of etched diffusion couples of $\text{Ti}_3\text{SiC}_2/\text{Zr-4}$ annealed at, a) 1100 °C for 1 h, b) 1200 °C for 10 h, and, c) $\text{Ti}_2\text{AlC}/\text{Zr-4}$ annealed at 1100 °C for 1 h. At the same conditions, the diffusion layer thicknesses observed for the $\text{Ti}_2\text{AlC}/\text{Zr-4}$ couples are almost an order of magnitude larger. Tunnel like pores are seen in the ZrSi layer in a). SEM micrograph d) of the etched $\text{Ti}_2\text{AlC}/\text{Zr-4}$ diffusion couple annealed at 1300 °C for 1 h shows TiC layers that formed surrounding the Ti_2AlC grains near the interface.

3.2 Ti_2AlC

At all temperatures studied, TAC formed numerous distinct layers, the thicknesses of which increased with annealing temperatures and times (Fig. 2). Table 2 summarizes the phases formed between Zr and TAC as a function of time and temperature. From the totality of these results it is reasonable to conclude that:

- i) The main intermetallic phases that form at all temperatures are Zr_2Al_3 and Zr_3Al_2 .
- ii) A layer with a consistent composition of 45% Al / 55% Zr, corresponding to Zr_5Al_4 , is also seen at all conditions, though nominally thinner than the layers described in i). The layer appears homogeneous; no precipitates can be seen (Fig. 2).
- iii) A thin Zr_3Al layer is observed closest to the Zr-4 side at all times at 1100 °C and after 1h at 1200 °C (Table 2). At higher temperatures, Zr_2Al is seen to form in addition, eventually replacing Zr_3Al all together at 1300 °C.
- iv) Deep into the Zr-4 and beyond the intermetallic layers, Zr_3Al precipitates decorate the grain boundaries of the β -Zr phase (Fig. 2). Additionally, the latter contains ≈ 8 at. % Al in solid solution. The solubility of 8 at. % corresponds to a temperature of about 900 °C, which suggests that is the temperature below which the diffusivities of Al in the β -Zr phase are too low. Interestingly and consistent with this interpretation is that the 8 at. % does not appear to be a function of annealing time or temperature. In other words, it is most probably determined upon cooling from the annealing temperature.
- v) In contrast to TSC/Zr-4, Ti from TAC was not seen to diffuse into the Zr-4. There was slight counter diffusion of Zr towards TAC.

Based on the aforementioned results it is reasonable to conclude that the overall reaction or diffusion path between TAC and Zr-4 is:

Phases shown in bold were present after all anneals. The Zr_2Al_3 layer was the thickest layer at all conditions (Fig. 2, Table 2). In contradistinction to the TSC/Zr-4 interfaces, the ones between Zr-4 and TAC, more often than not, fractured simply in handling the samples or after clamping them for sectioning. Transverse cracks were also more frequently observed in the intermetallic layers (Fig. 2). Both observations can be attributed to thermal stresses induced on cooling together with, presumably, the presence of a weak interface.

Table 2: Summary of phase compositions and their thicknesses, in μm , across the $\text{Ti}_2\text{AlC}/\text{Zr-4}$ diffusion couples – starting with Ti_2AlC – as a function of time and temperature. The last column lists the total thickness of the reaction layer and is the one plotted in Fig. 6.

Time (h)	Zr_2Al_3	Zr_5Al_4	Zr_3Al_2	Zr_2Al	Zr_3Al	Total Diffusion Thickness ‡
1100 °C						
1	39.3(4)	2.9(2)	5.5(2)	-	2.6(1)	50.3(7)
10	158(1)	10(1)	13.6(5)	-	4.5(2)	186(2)
30	212(2)	17(1)	30.7(7)	3.9(2)	4.5(1)	268(2)
1200 °C						
1	76.4(5)	4.6(3)	11.9(3)	2.4(1)	3.5(1)	99.3(8)
2	82.8(5)	7.1(3)	12.5(3)	-	6.9(3)	109.2(8)
10	142(1)	26(1)	23(1)	11(1)	-	201(2)
30	230(2)	48(2)	58(1)	9.7(8)	-	346(3)
1300 °C						
1	90.2(6)	9.7(3)	14.0(4)	10.4(5)	-	124(1)
10	147.7(6)	44.7(8)	58(1)	16(1)	-	267(2)
30	130(1)	114(1)	126(1)	19.7(9)	-	390(2)

‡ Does not include the region with Zr_3Al precipitates.

In some cases, the TAC grains deep in the MAX phase were surrounded by a thin white/grey layer, identified in SEM/EDX as TiC (Fig. 5d). Based on the extensive diffusion seen in Fig. 6b, the TiC layers did not appear to act as a diffusion barrier. Interestingly, no TiC

boundary layers were observed in the TSC samples, likely due to the significantly less Si diffusion from within the sample.

As shown in other studies of MAX joining [36-37], it is apparent that the Al from the TAC acts as a transient liquid phase, diffusing out of the basal planes in the grain boundaries (Fig. 5d) and readily diffusing throughout the Zr-4, that results in the growth of Zr_3Al precipitates along the Zr-4 grain far away from the interface (Fig. 2).

3.3 Comparison of the diffusion couples

There are a number of important similarities and differences between the results obtained from the various diffusion couples. In terms of similarities, in all cases, the main diffusing species is the A-group element. Given what is known about the reactivity of the A-group elements in the MAX phases this is far from surprising [8]. As early as 1999, it was shown that when Ti_3SiC_2 was immersed in cryolite, the Si was selectively etched by diffusing along the TSC grain boundaries [42]. Over the years the same was shown for other MAX phases in many environments. More recently it was shown that the Al can be etched out of the basal planes of Al-containing MAX phase by immersing their powders, at room temperature, in HF solutions [43]. At all temperatures there was some intermixing of the Ti and Zr atoms, suggesting at least some solubility of Zr in all these MAX phases. Under the conditions explored herein and within the resolution of our EDX measurements, limited C appears to have diffused into the Zr-4 or the intermetallics formed.

Since the solubility of Si in Zr is negligible, even at $T > 1600\text{ }^{\circ}C$, only a thin layer of Si in solution is detected beyond the intermetallic layers at $1200\text{ }^{\circ}C$, 2 and 10 h, and $> 10\text{ h}$ at $1300\text{ }^{\circ}C$. In sharp contradistinction the solubility of Al in Zr at $1200\text{ }^{\circ}C$ is of the order of 20 at.% [44].

It is presumably this significant solubility that accounts for the presence of Al deep beyond the intermetallic layers that form. Furthermore, at $T < 1019\text{ }^{\circ}\text{C}$, for Al concentrations $> 8\text{ at.}\%$ and $< 25\text{ }\%$, the equilibrium phase is Zr_3Al as observed in all cases. It is worth noting that while the initial Zr-phase was the α -Zr polymorph, after the high temperature anneals, it was transformed to β -Zr, as evidenced is the shape of the Zr grains after annealing that are clearly decorated by the Zr_3Al particles that precipitate along their grain boundaries (e.g. see Figs. 2 a, b, and c). The initial Zr-4 microstructure (not shown) is comprised of small equiaxed grains.

In all diffusion profiles, the Si and Al concentrations in the MAX phases are lower than their concentrations in the adjacent intermetallics (Figs. 3, 4). This uphill diffusion implies that the activities of the A-group elements in the MAX phases are considerably higher than their concentration would suggest. It is this enhanced activity that is responsible for crack healing in Ti_2AlC and Ti_3AlC_2 [45-47].

All else being equal, the diffusion layer thicknesses observed when Zr-4 was in contact with TAC were up to an order of magnitude larger than when it was in contact with TSC (Figs. 5a, c). This is especially noted in the $1200\text{ }^{\circ}\text{C}$, 30 h condition (Fig. 2b) where, at $346(3)\text{ }\mu\text{m}$, the intermetallic layer depth in TAC is an order of magnitude greater than TSC, at $36.9(7)\text{ }\mu\text{m}$ (Fig. 1b). Total diffusion distances (x) vs. $t^{1/2}$ for diffusion couples of Zr-4 with TSC (Fig. 6a) and TAC (Fig. 6b) in the temperature range of $1100\text{-}1300\text{ }^{\circ}\text{C}$ reveal that, for both materials, a linear fit with $t^{1/2}$ was observed, indicating that the diffusion obeyed a parabolic law in each case. The temperature dependence of the effective diffusion coefficients, D_{eff_A} , of the A-group elements through the reaction layers was fit to a linear regression of an Arrhenius plot (Fig. 6c). For TSC/Zr-4, the temperature dependence is described by:

$$D_{eff_Si}(\frac{m^2}{s}) = 7.4 \times 10^{-9} \exp(\frac{-170 \text{ kJ/mol}}{RT}), \quad (3)$$

and for TAC/Zr-4, the temperature dependence is described by:

$$D_{eff_Al}(\frac{m^2}{s}) = 9.2 \times 10^{-12} \exp(\frac{-38 \text{ kJ/mol}}{RT}). \quad (4)$$

At 38 kJ/mol, the activation energy for D_{Al} is significantly lower than the 170 kJ/mol of D_{Si} . These results for TSC/Zr-4 compare well with previous diffusion studies, where activation energies of various diffusion couples were reported as 118, 132, and 156 kJ/mol for TSC/Ni [48], TSC/Si [49], and TSC/Ti-6Al-4V [36], respectively.

Figure 6. Total diffusion distance (x) vs. $t^{1/2}$ for diffusion couples of: a) Ti₃SiC₂ and, b) Ti₃AlC₂ with Zr-4 in the temperature range of 1100-1300 °C. In all cases, Ti₃SiC₂ results in a shallower diffusion length. These trends show a parabolic diffusion behavior as $x \approx (2Dt)^{1/2}$. c) Arrhenius plot of the effective diffusion coefficients, D_{eff_A} .

In general, and under all conditions tested, the diffusion layer thicknesses observed were larger when Al was present in the system than when Si was. Figures 5a and c compare SEM micrographs of diffusion couple interfaces between Zr-4, on the one hand, and TSC and TAC on the other, respectively. Despite the relatively short diffusion time of 1 h and the relatively low

diffusion temperature (1100 °C) it is obvious that the Si penetration depth in the Zr-4 is significantly less than Al. This difference is more dramatically realized when Zr-4 and TAC were diffusion bonded at 1300 °C for 30 h (Figs. 1c and 2c) are compared. The reaction layer thickness in the TAC case was of the order of 390 μm . The reaction layer thickness that formed under identical conditions when TSC was in contact with Zr-4 was $\sim 75 \mu\text{m}$ (Fig.1c).

4. Summary and Conclusions

The reactivity between Zr-4 and Ti_3SiC_2 and Ti_2AlC , over the 1100-1300 °C temperature range, was studied by setting up TSC/Zr-4 and TAC/Zr-4 diffusion couples. Based on the results shown, and similar to previous work in the Zr/Al system, it is clear that Al-diffusion into Zr was extensive, and resulted in a large affected diffusion zone with several Zr_xAl_y intermetallic layers [31-33]. Zr_3Al precipitates were observed up to 200 μm into the Zr-4 bulk after annealing at all conditions. The Al diffused out of the TAC basal planes and through the grain boundaries, resulting in the formation of TiC rings around TAC grains near the bonding interface.

Diffusion of Si from TSC generally formed two intermetallic layers: ZrSi and Zr_3Si . At higher temperatures, layers of ZrSi_2 , Zr_3Si_2 , and Zr_2Si also formed. In this case, TiC layers were not seen to form around any of the TSC grains.

Overall, diffusion depths from Ti_3SiC_2 were an order of magnitude shallower than the Al-containing MAX phases at 1100 and 1200 °C, and 5-7 times shallower at 1300 °C. The diffusion of both Si and Al is seen to follow the parabolic law, and the microstructure of the diffusion bonded regions is indicative of the diffusion controlled reaction.

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