Stability of V_2AlC with Al in 800 to 1000 °C temperature range and *in situ* synthesis of V_2AlC/Al composites

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1. Introduction

The MAX phases are a family of nanolayered, machinable, ternary carbides and nitrides, having the general formula $M_{n+1}AX_n$ – where $n = 1, 2, 3$; M is an early transition metal; A is an A-group element (mostly groups 13 and 14); and X is C and/or N [1]. These phases combine some of the best properties of metals and ceramics. Like metals they are machinable, electrically and thermally conductive [2, 3], damage tolerant and not susceptible to thermal shock [4]. Like ceramics, some of them are lightweight ($\approx 4 \text{ Mg/m}^3$) and elastically rigid (Young's moduli $> 300 \text{ GPa}$). These unique properties render the MAX phases desirable candidates for use as reinforcement phases in metal matrix composites, MMCs.

Recently, magnesium, Mg, matrix composites reinforced with Ti_2AlC – a member of the MAX phases - have been developed [5]. These Mg and Mg alloys-MAX composites were manufactured by spontaneous melt infiltration, MI, of porous MAX preforms, at relatively low processing temperatures (750°C) yielding composites with attractive mechanical properties. For example, the Young's modulus and ultimate compressive strengths, UCSs, of a Mg alloy (AZ61) matrix composite reinforced with 50 vol. % Ti_2AlC particles were found to be $136\pm6 \text{ GPa}$ and $760\pm9 \text{ MPa}$, respectively. In addition to the excellent mechanical properties, these composites dissipated almost 25 % of the applied mechanical energy at high stresses [5]. The resulting composites were also most readily machinable, since both constituents are machinable. These promising results spurred interest in developing Al-MAX composites with comparable or better properties.

Fabricating Al-matrix MAX reinforced composites is complicated by the fact that Al is not in equilibrium with most MAX phases [1]. For example, Wang et al. [6] attempted to

fabricate Ti_3AlC_2 composites at elevated temperatures and found that above 950°C , Ti_3AlC_2 reacted with Al to form TiC and TiAl_3 . To circumvent this problem Wang et al. [6] hot pressed Al and Ti_3AlC_2 powders at a temperature (550°C) at which the reaction kinetics were slow. Similarly, our attempt to synthesize an Al- Ti_2AlC composite by melt infiltration was thwarted by: i) the low wetting of Al into porous Ti_2AlC preforms at, and below, 1000°C , ii) reaction between Al and Ti_2AlC above 1000°C , and, iii) low temperature reaction (900°C) between Al and Ti_2AlC when infiltration kinetics were increased by the addition of B_4C [7]. More successfully, Hu et al. [8] used current-activated, pressure-assisted infiltration to fabricate Al- Ti_2AlC composites. In this method, the processing and densification occur too rapidly for extensive reactions to occur. Their nearly full dense composites were lightweight, with UCS's of the order of 500 MPa. At $160\text{ MPa cm}^3/\text{g}$, their specific strengths were approximately 4 times higher than those of pure Al [8]. These solutions to the problem, however, do not lend themselves to scalable, inexpensive manufacturing.

One MAX phase that has been reported to be in equilibrium with liquid Al at 1000°C is V_2AlC [9]. However, the extent of its thermodynamic stability and its use as a reinforcement phase in Al MMCs has remained uninvestigated. Herein we report on the stability of V_2AlC in liquid Al at temperatures below 1000°C and on the fabrication of Al- V_2AlC composites. Before doing so, it is important to review the following phase diagrams.

1.1. Phase diagrams

1.1.1. Al-C system

The only binary phase in the Al-C system is Al_4C_3 , a phase that has been reported to be stable to above 2100°C [10]. The solubility of C in Al is negligible in the temperature range used herein [10].

1.1.2. V-C system

The stable phases at 1000 °C are V_2C , VC_{1-x} , V_6C_5 , and V_8C_7 . These phases have all been well characterized [11]. The only other phase known to exist in this system is V_4C_{3-y} at temperatures between 1260 and 1870 °C. In 2010, Okamoto [12] provided the most current assessment of the V-C phase diagram.

1.1.3. Al-V system

In the latest review of the Al-V phase diagram, [13] Al_3V and Al_8V_5 are equilibrium phases at 1000 °C. The Al-rich phases – $Al_{23}V_4$, $Al_{45}V_7$ and $Al_{21}V_2$ – only exist below 734 °C, when Al_3V falls out of equilibrium with liquid Al (Fig. 1). The V-rich side of the phase diagram is primarily a V-Al solid solution above ≈ 50 -60 at.% V. The ordered phase AlV_3 is shown to exist; however, discrepancies between studies have been noted [14].

1.1.4. V-Al-C system

Schuster et al. [9] investigated the full V-Al-C compositional range at 1000 °C (Fig. 2a). The only ternary phase reported is the MAX phase, V_2AlC . The latter is found to exist in equilibrium with liquid Al, the V-Al solid solutions and all the binary phases, but not with C. More recently, Etzkorn et al. reported on the existence of the V_4AlC_3 phase in this system.[15]

The aim of this work was to synthesize Al- V_2AlC composites and to investigate the phase equilibrium between Al and V_2AlC at temperatures and compositions typical for the fabrication these composites.

2. Experimental Details

2.1. Materials

Pure Al (99.5%, -325 mesh, Alfa Aesar, Ward Hill, MA), V (99.5%, -325 mesh, Alfa Aesar, Ward Hill, MA) and graphite (99%, -325 mesh, Alfa Aesar, Ward Hill, MA) powders were used in this work.

2.2. Processing

2.2.1. Preparation of Al-MAX composites

Two composites were fabricated starting with elemental powders. The first composite, henceforth referred to as AlR, was more Al-rich, having a nominal Al:V:C molar ratio of 9.8:2.0:1.0. The second composite, henceforth referred to as VR, was more V-rich, having the nominal Al:V:C molar ratio 3.9:2.0:1.0. These compositions were chosen so that *in situ* formation of V_2AlC would produce MMCs having ≈ 25 vol% and ≈ 50 vol. % V_2AlC reinforcement in the AlR and VR samples, respectively (Fig. 2b).

The powder mixtures were ball milled for 16 h with yttria stabilized zirconia grinding media. Approximately 10 g of each mixture was cold pressed in a steel mold ($6.1 \times 12.7 \text{ mm}^2$) - to a load corresponding to a stress of 200 MPa - to form rectangular preforms, which were then cut into 5 equal pieces (≈ 2 g each). The preforms were placed in alumina crucibles (AdValue Technology, Tucson, AZ) and heated at a rate of $10^\circ\text{C}/\text{min}$ to 1000°C and allowed to soak for 0.5, 2.5 or 10 h. All experiments were carried out in a horizontal tube furnace under flowing argon, Ar, gas at atmospheric pressure. One sample of each the AlR and VR composition, annealed for 10 h, was allowed to furnace cool to room temperature. For reasons that will become clear shortly, all other samples were quenched in a water bath. To do so, the furnace was opened and the samples were grabbed by tongs and within ≈ 5 s of being removed from the hot-zone of the tube furnace they were quenched in a water bath held at room temperature. Henceforth, the AlR and VR composites that were furnace cooled will be referred to as AlR-FC

1 and VR-FC, respectively; those that were water quenched will be referred to as AlR-WQ and
2 VR-WQ, respectively.

3 The relative densities of the various samples were measured using the Archimedes
4 method. It was assumed that the volume fractions of V_2AlC and Al were 25/75 vol.% and 50/50
5 vol.% for the AlR and VR samples, respectively. The constituent densities used in this
6 calculation were 4.81 g/cm^3 for V_2AlC [16] and 2.70 g/cm^3 for Al [17]. This approximation was
7 validated after Rietveld refinements provided accurate volume fractions (see below). The change
8 in relative density after accounting for impurities was negligible. X-ray diffraction (XRD) and
9 scanning electron microscopy (SEM) were used for phase analysis and microstructure
10 characterization, and differential scanning calorimetry (DSC) was used to identify the various
11 reaction temperatures in the composites made.

12 *2.2.3. Preparation of samples for DSC*

13 In order to evaluate the stability of V_2AlC with Al below 1000°C , a master alloy, MA,
14 having a nominal Al:V:C composition of 24.2:4.4:1.0 (Figs.2b and c), was prepared. The
15 powders were mixed, pressed and heated in the same manner as the other experiments. One
16 sample, henceforth referred to as MA-FC, was allowed to furnace cool after soaking at 1000°C
17 for 10 h; the other sample, henceforth referred to as MA-WQ, was water quenched. The MA-FC
18 sample was subsequently analyzed using DSC. The MA-WQ sample was divided into thirds.
19 One part was analyzed using DSC. Another piece was equilibrated for 10 h at 800°C under
20 flowing Ar, water quenched and analyzed by XRD. The last piece was equilibrated in the same
21 manner at 1000°C , water quenched and analyzed by XRD. Rietveld analysis of the XRD spectra
22 gave the Al:V:C molar compositions of 15.3:2.6:1.0 and 13.5:3.0:1.0 for the samples equilibrated

at 800 and 1000 °C, respectively (Figs. 2b and c). The details of the various tests are summarized in Fig. 2c.

2.3. Characterization

2.3.1. X-ray diffraction

Powders for XRD were obtained by drilling the composites with a carbide drill bit and analyzed using a X-ray diffractometer (Rikagu Smartlab, Japan). The angular step was set to 0.02° over the $2\theta = 5^\circ - 80^\circ$ range, with a hold time of 0.5 s for the AIR-FC and VR-FC samples. For the AIR-WQ and VR-WQ samples, the angular step was set to 0.02° over the $2\theta = 20^\circ - 50^\circ$ range, with a hold time of 1.5 s. The MA-FC and MA-WQ samples used the same angular step over the $2\theta = 20^\circ - 80^\circ$ range, with a hold time of 1.0 s. Scans were made through a 10x10 mm² window slit using Cu K α radiation (40 KV and 30 mA). Jade XRD pattern recognition software (Materials Data, Inc., Livermore, CA.) was used to analyze the XRD results. Rietveld refinements of some of the XRD patterns were conducted using *FullProf* [18]. Refined parameters were: six background parameters, lattice parameters of all phases, scale factors from which relative phase fractions are evaluated, and X profile parameters for peak width.

2.3.2. Scanning electron microscopy

After cross-sectioning, mounting, and polishing (1200 grit), the microstructures of select composites were imaged using a scanning electron microscope, SEM, (Zeiss Supra 50VP, Germany) equipped with an energy-dispersive spectroscopy, EDS, (Oxford Inca X-Sight, Oxfordshire, UK). The EDS spectra were taken at a working distance of 12 mm and an accelerating voltage of 15 kV.

2.3.3. Differential scanning calorimetry

Approximately 225 mg of the MA-WQ sample and 228 mg of the MA-FC sample were analyzed using a DSC (SDT Q600, TA Instruments, New Castle, DE). The heating/cooling rate was 10 °C/min over the 100 – 1000 °C temperature range. Data points were collected every 0.6 s.

3. Results

3.1. Al-MAX Composites

After reacting the powder compacts at 1000°C, the resulting sintered bodies were not dense. The densities of the water quenched AlR samples were ≈ 90 % of theoretical, with no apparent relation between annealing times and density. For the VR samples, the relative density ranged from 30 to 60 %. Here again, no trends with annealing times were observed. Due to their lower relative densities, the VR samples could be easily crushed by hand and could not be polished for microscopy.

The predominantly two-phase nature of both the AlR and VR composites, after quenching from 1000 °C, was confirmed by both XRD (Fig. 3) and SEM (Figs. 4 and 5) investigations. Rietveld analysis of the XRD spectra for the water quenched AlR composites (Fig. 3a) yielded the following volume fractions: Al = 71.6 vol.% (60.0 wt.%), V_2AlC = 22.6 vol.% (33.7 wt.%) and Al_3V = 5.8 vol.% (6.3 wt.%). The same analysis for the water quenched VR composites (Fig. 3b) yielded the following volume fractions: Al = 49.6 vol. % (35.6 wt.%) and V_2AlC = 50.4 vol. % (64.4 wt.%). The χ^2 values of the Rietveld refinements of the XRD patterns for the AlR and VR composites (Fig. 3) were 3.40 and 1.34, respectively.

Large pores could be seen at low magnifications of the AlR-WQ composite (Fig 4a). EDS of this sample showed that the compositions of the two existing phases corresponded to V_2AlC and an Al matrix, with some grains having a composition close to Al_3V (Fig. 4b). Sintered Al particles, that did not form part of the continuous matrix, could be seen at higher magnifications (Fig. 4c).

SEM of the water quenched VR composite samples clearly demonstrated their porous nature (Fig. 5a). V_2AlC was clearly identified from EDS and was again found dispersed among an Al matrix (Fig. 5b).

Somewhat surprisingly, the XRD patterns of the AlR and VR samples allowed to furnace cool after 10 h at 1000 °C (Fig. 6) were quite different than the ones that were water quenched (Fig. 3). The furnace cooled AlR samples were primarily comprised of Al_3V and Al-rich intermetallics ($Al_{23}V_4$, $Al_{45}V_7$ and $Al_{21}V_2$), with trace amounts of Al_4C_3 (Fig. 6a). The furnace cooled VR samples, were comprised of V_2AlC , Al_3V and some Al_4C_3 (Fig. 6b).

3.2. Differential scanning calorimetry

The DSC results for the MA-WQ sample (Fig. 7) exhibited 2 distinct exothermic peaks (labeled as P1 and P2, respectively, in Fig. 7a) and 1 endothermic peak (labeled P3 in Fig. 7a) during heating. Only one exothermic peak was observed during cooling (labeled P4 in Fig. 7b). Additionally, a small possible endothermic peak was identified at the leading edge of P1 at 659 °C (Fig. 7a). The maximum of P1 occurred at $T = 685$ °C. Peak, P2, had an onset temperature of approximately 731 °C and reached a maximum at 739 °C. The endothermic peak, P3, began when $T \approx 940$ °C and ended by $T \approx 970$ °C. The only peak observed during cooling, P4, began at

1 $T \approx 922\text{ }^{\circ}\text{C}$ and ended at $T \approx 896\text{ }^{\circ}\text{C}$. Note the similar magnitudes and ranges of the P3 and P4
2 peaks. Their areas were calculated to be the same within 10 % of each other.

3 The DSC curve for the furnace-cooled sample, MA-FC (Fig. 8a) exhibited three small
4 endothermic peaks (labeled π_1 , π_2 and π_3 , respectively, in Fig. 8a), one sharp exothermic peak
5 (labeled π_4 in Fig. 8a) and a larger endothermic peak (labeled π_5 in Fig. 8a) during heating.
6 During cooling, two exothermic peaks were identified (π_6 and π_7 in Fig. 8b). The minimum of
7 π_1 occurred at $660\text{ }^{\circ}\text{C}$ and spanned the $657 - 666\text{ }^{\circ}\text{C}$ temperature range. The onset temperature
8 of π_2 was $\approx 686\text{ }^{\circ}\text{C}$ and spanned to a $T \approx 695\text{ }^{\circ}\text{C}$. The peak π_3 was found to be broader than π_1
9 or π_2 , spanning from $\approx 710-740\text{ }^{\circ}\text{C}$, with the minimum occurring at $= 727\text{ }^{\circ}\text{C}$. The exothermic
10 peak, π_4 , had a maximum at $814\text{ }^{\circ}\text{C}$, spanning the $798 - 829\text{ }^{\circ}\text{C}$ temperature range $^{\circ}\text{C}$. The larger
11 endothermic peak, π_5 , began at $940\text{ }^{\circ}\text{C}$ and ended by $995\text{ }^{\circ}\text{C}$, the minimum occurred at $968\text{ }^{\circ}\text{C}$.
12 This peak was similar in magnitude to the exothermic peak, π_6 , that began during cooling at 935
13 $^{\circ}\text{C}$ and continued to $887\text{ }^{\circ}\text{C}$. Again, note the similarities between the exothermic π_5 and
14 endothermic π_6 peaks. Their areas were calculated to be the same within 10 % of each other. A
15 second small exothermic peak observed during cooling, π_7 , began at $657\text{ }^{\circ}\text{C}$, reached a
16 maximum at $651\text{ }^{\circ}\text{C}$ and was ended by $636\text{ }^{\circ}\text{C}$.

17 After equilibration of the MA-WQ sample at 800 and $1000\text{ }^{\circ}\text{C}$, XRD was used to
18 establish the phases present (Fig. 9). After water quenching from $800\text{ }^{\circ}\text{C}$, the phases present were
19 Al, Al_3V and Al_4C_3 (Fig. 9a). After water quenching from $1000\text{ }^{\circ}\text{C}$, the phases present - Al, Al_3V
20 and V_2AlC (Fig. 9b) – were the same as those reported by Schuster, et al. who also quenched
21 their samples.[9]

22 **4. Discussion**

4.1. Al-MAX Composites

The most important practical implication of this work is that two-phase Al-V₂AlC composites can be readily made via an *in situ* reaction followed by quenching from 1000 °C (Fig. 3). The volume fractions of the AlR-WQ and VR-WQ composites, as determined from Rietveld analysis, were similar to those expected from their nominal compositions. Further work, however, is required, and ongoing, to increase the relative densities of these composites. As importantly, we mapped out the Al-rich corner of the Al-V-C ternary phase diagram at 800 °C (Fig. 2b) and find that, in contrast to the phase diagram at 1000 °C (Fig. 2a), Al and V₂AlC are in equilibrium with Al₄C₃ and Al₃V, but not with each other. This insight explains why quenching from T > 950 °C is required to make Al-V₂AlC composites.

4.2. Phase stability and reaction paths

The starting phases in the MA-WQ sample were V₂AlC, Al, and Al₃V; these are the phases present in region 1 (Fig. 7) as confirmed by XRD (Fig. 9b). The exothermic peak, P1 at 685 °C, may first seem surprising, since pure Al melts 660 °C. However, given what we now know about the instability of V₂AlC in Al at T < 950 °C, this peak is most likely due to the decomposition of V₂AlC into Al₄C₃ and Al-rich intermetallics according to the following reactions:

and

Note that the exothermic nature of these reactions is consistent with the reduction of entropy upon reaction. Also note that the small endothermic peak at the shoulder of P1 (Fig. 7) may be related to the melting of Al. This endothermic process is probably masked by reactions 1 and 2.

The temperatures that P1 span (660 – 700 °C) agree with the temperatures reported for the existence of $Al_{21}V_2$, $Al_{45}V_7$ and $Al_{23}V_4$ (Fig. 1). [13] As our system is more V-rich, $Al_{23}V_4$ is expected to be the equilibrium phase.

Following the decomposition of V_2AlC , region 2 in Fig. 7, likely contains the phases Al_4C_3 , Al_3V and $Al_{23}V_4$. The melting of the Al-rich intermetallic to form liquid Al and Al_3V ($T = 734$ °C in Fig. 1) may be clearly identified as P2, and proceeds according to the reaction:

Region 3 then contains Al_4C_3 , Al_3V and liquid Al. These phases remain stable until P3 ($T \approx 938$ °C), at which point Al_4C_3 and Al_3V react to form V_2AlC and liquid Al, according to:

Region 4 is then in agreement with the reported ternary phase diagram at 1000 °C (Fig. 2a). [9]

Upon cooling, reaction 4 runs in reverse and gives rise to the exothermic peak P4 at 924 °C. Region 5 then has the same stable phases as region 3. The observed hysteresis (different temperature ranges between P3 and P4) may be attributed to an activation energy necessary to initiate the reaction.

The lack of any other peaks during cooling, especially below 800 °C, is unexpected, as liquid Al should solidify at 660 °C. Why an exothermic peak at that temperature was not observed is unclear at this time. However, it is possible that any excess Al slowly oxidized during testing such that no liquid Al existed during cooling. This hypothesis was corroborated by a small increase in mass (1.2 wt. %) and XRD patterns of the DSC sample after testing, which showed notable Al₂O₃ and no Al peaks.

The starting phases – those present in region 1 in Fig. 8 - in the MA-FC sample were Al₄C₃, Al₃V and Al-rich intermetallics (predominantly Al₂₃V₄). The small endothermic peaks, π_1 - π_3 , agree well with the peritectic temperatures of the Al intermetallics and the three phases can be ascribed to the following reactions:

Therefore, in region 2 (Fig. 8), the phases present are Al₄C₃, Al₃V, Al₂₃V₄, and liquid Al. In other words, the phases present are similar to those in region 2 in Fig. 7. It follows that the sharp exothermic peak, π_4 , must be due to reaction Eq. 3. The reason this peak is shifted up by 70 °C, compared to its position in the MA-WQ sample, is unclear at this time. The first peak observed during cooling, π_6 , is similar to peaks π_5 and to P4 in Fig. 7, and confirms the reversibility of Eq. 4 in this sample. Lastly, π_7 shows that some liquid Al did solidify below T = 660 °C. The change in mass of this sample was < 0.3 wt. %, indicating that oxidation may not have been as severe.

4.3. Phase equilibria

Based on the totality of our XRD (Fig. 9a), SEM and DSC (Fig. 7) results of the equilibrated MA-WQ composition at 800 °C, it is reasonable to conclude that the 3 apexes of this equilibrium triangle are: Al, Al₃V and Al₄C₃. An isothermal section of the Al-V-C phase diagram, in the Al-rich corner, can thus be drawn for 800 °C (Fig. 2b). The starting molar composition (red square in Fig. 2b), clearly falls within this equilibrium triangle. XRD after equilibration at 1000 °C (Fig. 9b) confirmed the phase relations – Al, Al₃V and V₂AlC – reported by Schuster et al. [9]

The agreement between the nominal MA composition (red square in Fig. 2b) and the composition as determined by Rietveld analysis (blue circle in Fig. 2b) of the MA-WQ sample equilibrated at 800 °C is good. The discrepancy between the nominal starting molar composition (red square in Fig. 2b) and the composition as determined by Rietveld analysis of the sample equilibrated at 1000 °C (purple diamond in Fig. 2b) is probably due to the evaporation of some Al during the 10 h equilibration anneal at 1000 °C. This comment notwithstanding, since each composition resides within its *pertinent* equilibrium triangle at 800 °C (Al, Al₃V, Al₄C₃) and 1000 °C (Al, Al₃V, V₂AlC), this discrepancy in no way affects the conclusions of this study.

Lastly we note that we made use of the fact that the equilibrium temperature for reaction 4, was 1211 K, to calculate the enthalpy and free energies of formation for V₂AlC in the 0 to 1400 K temperature range. This work has been accepted for publication.

4. Summary

- The synthesis of Al-V₂AlC composites was achieved by quenching from 1000 °C after soaking for 0.5, 2.5 or 10 h. Furnace cooled samples did not produce Al-V₂AlC

composites. These results imply Al-V₂AlC can be easily fabricated by reaction sintering at T > 950 °C, followed by quenching and that those composites would be stable up to ≈ 500 °C.

- Differential scanning calorimetry demonstrated that V₂AlC was unstable in liquid Al below ≈ 950 °C, with the following reaction: $19 \text{ Al} + 3 \text{ V}_2\text{AlC} \Rightarrow \text{Al}_4\text{C}_3 + 6 \text{ AlV}_3$ occurring.
- The 800 °C isothermal section of the Al-V-C phase diagram in the Al-rich corner has been determined for the first time. At 800 °C, both Al and V₂AlC were found to be in equilibrium with Al₃V and Al₄C₃, but *not* with each other.

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References

- [1] M.W. Barsoum, MAX Phases: Properties of Machinable Ternary Carbides and Nitrides, John Wiley & Sons, 2013.
- [2] M.W. Barsoum, T. ElRaghy, Synthesis and Characterization of a Remarkable Ceramic: Ti₃SiC₂, J. Am. Ceram. Soc., 79 (1996) 1953-1956.
- [3] M.W. Barsoum, D. Brodtkin, T. ElRaghy, Layered Machinable Ceramics for High Temperature Applications, Scripta Mater., 36 (1997) 535-541.
- [4] M.W. Barsoum, M.C. Flemings, E.J. Kramer, S. Mahajan, P. Veyssiere, Physical Properties of the MAX Phases, In: Encyclopedia of materials science and technology, (2006).
- [5] B. Anasori, E.N. Caspi, M.W. Barsoum, Fabrication and Mechanical Properties of Pressureless Melt Infiltrated Magnesium Alloy Composites Reinforced with TiC and Ti₂AlC Particles, Materials Science and Engineering: A, 618 (2014) 511-522.

- [6] W.J. Wang, V. Gauthier-Brunet, G.P. Bei, G. Laplanche, J. Bonneville, A. Joulain, S. Dubois, Powder Metallurgy Processing and Compressive Properties of Ti₃AlC₂/Al Composites, Materials Science and Engineering: A, 530 (2011) 168-173.
- [7] M. Agne, B. Anasori, M. Barsoum, Reactions Between Ti₂AlC, B₄C, and Al and Phase Equilibria at 1000 °C in the Al-Ti-B-C Quaternary System, Journal of Phase Equilibria and Diffusion, 36 (2015) 169-182.
- [8] L. Hu, A. Kothalkar, M. O'Neil, I. Karaman, M. Radovic, Current-Activated, Pressure-Assisted Infiltration: A Novel, Versatile Route for Producing Interpenetrating Ceramic–Metal Composites, Materials Research Letters, (2014) 1-7.
- [9] J. Schuster, H. Nowotny, 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 (1980) 213-219.
- [10] C. Qiu, R. Metselaar, Solubility of Carbon in Liquid Al and Stability of Al₄C₃, J. Alloys Compd., 216 (1994) 55-60.
- [11] O.N. Carlson, A.H. Ghaneya, J.F. Smith, The C–V (Carbon-Vanadium) system, Bulletin of Alloy Phase Diagrams, 6 (1985) 115-124.
- [12] H. Okamoto, C-V (Carbon-Vanadium), Journal of Phase Equilibria and Diffusion, 31 (2010) 91-92.
- [13] H. Okamoto, Al-V (Aluminum-Vanadium), Journal of Phase Equilibria and Diffusion, (2012) 1-1.
- [14] J.L. Murray, Al-V (aluminum-vanadium), Bulletin of Alloy Phase Diagrams, 10 (1989) 351-357.
- [15] J. Etzkorn, M. Ade, H. Hillebrecht, V₂AlC, V₄AlC_{3-x} (x≈ 0.31), and V₁₂Al₃C₈: synthesis, crystal growth, structure, and superstructure, Inorg. Chem., 46 (2007) 7646-7653.
- [16] Z. Sun, S. Li, R. Ahuja, J.M. Schneider, Calculated elastic properties of M₂AlC (M= Ti, V, Cr, Nb and Ta), Solid State Commun., 129 (2004) 589-592.
- [17] R.B. Ross, Metallic materials specification handbook, Springer Science & Business Media, 2013.
- [18] J. Rodríguez-Carvajal, Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction, Physica B: Condensed Matter, 192 (1993) 55-69.

Figure 1. Al-rich corner of the Al-V binary phase diagram. [13]

Figure 2. (a) Isothermal Al-V-C ternary phase diagram at 1000 °C [9] and, (b) at 800 °C for the Al-rich corner determined herein. The locations of the nominal AlR and VR compositions are labeled accordingly. The nominal composition of the MA samples is shown as the open red square; the same composition as determined by Rietveld analysis after equilibration at 800 °C is shown by an open blue circle and after equilibration at 1000 °C by an open purple diamond. (c) Flow chart showing heat treatments and various characterization tests carried out on the MA-FC and MA-WQ samples whose compositions are those shown in Fig. 2b.

Figure 3. Typical XRD patterns of, a) AlR and, b) VR composites after annealing for 10 h at 1000 °C, and subsequently water quenched.

Figure 4. Secondary electron SEM images of a water quenched AlR composite after soaking at 1000 °C for 2.5 h showing, (a) two phase nature of the composite and the presence of some large pores throughout. (b) same as A but at higher magnification and, (c) the presence of sintered Al particles that did not appear to be part of the continuous Al matrix (marked by double arrows).

Figure 5. Secondary electron SEM images of a water quenched VR composite after soaking at 1000 °C for 2.5 h showing, (a) sample porosity, and, (b) clumps of V_2AlC grains held together by Al particles (left hand side), verified by backscattered electron SEM image (right hand side).

Figure 6. Typical XRD patterns for furnace cooled, a) AlR and, b) VR compositions. Both patterns are quite different from those of the same compositions that were water quenched (see Fig. 3).

Figure 7: DSC curve for the MA-WQ sample during, a) heating (top red) and, b) cooling (bottom blue). Two exothermic and one endothermic peak were registered during heating, but only one exothermic peak during cooling. The heating and cooling curves are separated for clarity. The vertical offsets from 0 are +200 and +100 for the heating and cooling curves, respectively.

Figure 8: DSC curve for the MA-FC sample during, a) heating (top red) and, b) cooling (bottom blue). Several small (see inset) and one large exothermic peak and one endothermic peak were registered during heating, and two exothermic peaks during cooling. The heating and cooling curves are separated for clarity. The linear offsets from 0 are +200 and +100 for the heating and cooling curves, respectively.

Figure 9. Diffraction patterns of MA-WQ sample after equilibration and quenching at, a) 800 °C and, b) 1000 °C.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9