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Molten salt synthesis of MAX phases in the Ti-Al-C system

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Abstract

The molten salt method was used to synthesise the MAX phase compounds Ti₂AlC and Ti₃AlC₂ from elemental powders. Between 900–1000 °C, Ti₂AlC was formed alongside ancillary phases TiC and TiAl, which decreased in abundance with increasing synthesis temperature. Changing the stoichiometry and increasing the synthesis temperature to 1300 °C resulted in formation of Ti₃AlC₂ alongside Ti₂AlC and TiC. The type of salt flux used had little effect on the product formation. The reaction pathway for Ti₂AlC was determined to be the initial formation of TiC_{1-x} templating on the graphite and titanium aluminides.

Keywords: Ti₂AlC, Ti₃AlC₂, MAX phase, molten salt, synthesis

1. Introduction

MAX phases are layered compounds with the space group $P6_3/mmc$ formed from at least one transition metal (M), at least one metalloid element (A) and a non-metal (X), principally carbon or nitrogen. They are primarily considered to conform to the general formula $M_{n+1}AX_n$ and the nomenclature 211, 312 and 413 refer to the three simplest MAX phase formulae [1]. A number of other formula relationships exist for compounds of M, A and X elements which have similarities to those corresponding to the $M_{n+1}AX_n$ formulae but are not considered as true MAX phases but rather as 'MAX phase-like' [2]. Alloying of one or more elements within the M and/or A sublattices is also possible and potentially also the X sublattice, giving a very wide range of potential compositions beyond the 60 or so true MAX phases discovered composed from only three elements [3].

MAX phases were originally discovered/synthesised in the 1960s, but subsequently were little researched until their remarkable combination of properties was identified in the 1990s including relatively high fracture toughness compared to ceramics, machinability and good thermal and electrical conductivity; bridging the gap between metallic and ceramic materials [4]. They are now extensively researched. Typically, MAX phases have reasonable oxidation resistance, but in particular aluminium-containing phases have been shown to form a well-adhered protective alumina (Al₂O₃) scale upon heating in air, which does not spall off with heat-cycling [5] further protecting the underlying material. Due to their properties, these materials currently find use in furnace tubes, heating elements, burner nozzles and in other refractory applications [1], [5]. Nuclear applications are also being investigated including as part of the fuel cladding and as part of the pump impeller in liquid metal-cooled reactors [6], [7].

Ti₂AlC and its '312' counterpart Ti₃AlC₂ are well documented MAX phases and have previously been synthesised through a number of routes. Ti₂AlC thin films were first produced by Jeitschko, Nowotny and Benesovsky in 1963 [8]. Zhou et al. made dense Ti₂AlC pellets at 1100 °C using spark plasma sintering (SPS) [9], while Barsoum, Ali and El-Raghy achieved high purity bulk samples through hot pressing at 1300 °C [10]. Although discovered by Pietzka and Schuster [11], Ti₃AlC₂ was first characterised by Tzenov and Barsoum, using bulk samples synthesised by hot pressing [12]. The phase has also been synthesised through SPS by Zhou, Wang and Hunang [13] at 1250 °C and by Mizuno et al. at 1300 °C [14]. Chen et al. formed the phase through a novel method of rapid melting with a 5kW laser, allowing for synthesis in the order of minutes [15].

Compared to hot pressing and SPS, the molten salt method is relatively unexplored for MAX phase synthesis. This process involves the addition of a large amount of salt to the precursor materials, which then melts in the furnace. The molten salt flux helps to dissolve reactants and increase diffusion, ultimately aiding synthesis [16]. The salt can then be washed from the crushed sample, resulting in a fine polycrystalline powder. In 2013, Guo et al. formed Ti₃SiC₂ from elemental powders in molten NaCl, reporting a synthesis temperature 150 °C lower than other methods [17]. Tian et al. reported on the creation of Cr₂AlC under vacuum using molten salts at 1000 °C [18].

During molten salt synthesis, two possible reaction mechanisms can occur: dissolution-precipitation occurs if multiple reactants dissolve in the salt, react and precipitate out of the salt, which will give the product a morphology independent of the starting materials [19]; the other mechanism involves one or more reactants dissolving in the salt, and forming the product as a precipitate on the surface of an insoluble reactant. This templating will give resulting particles a morphology that is dependent on the reactant morphology, which can allow tailoring of the product.

2. Materials and methods

Powders of titanium (74 µm, 99.5% pure, Alfa Aesar), aluminium (44-420 µm, 99.8% pure, Alfa Aesar) and graphite (44 µm, 99% pure, Alfa Aesar) were used as the starting materials, along with NaCl (99.5% pure, Alfa Aesar) and KCl (99% pure, Sigma Aldrich) as the salt flux. Two molar ratios were used: "TAC2" (2:1.2:1 of Ti:Al:C) and "TAC3" (3:1.2:2 of Ti:Al:C). These two mixtures were intended to synthesize both Ti₂AlC and Ti₃AlC₂ respectively. Excess aluminium was added to decrease the effect of its partial loss at high temperature, in line with common practice when producing MAX phases, recognising the often higher volatility of A elements. Experiments were performed using one of three fluxes: NaCl, KCl, and an equal mixture of the two known as "NaKE". The latter forms a low temperature eutectic phase, melting at 658 °C [20] which closely matches the melting point of aluminium. It was hoped that this would further aid diffusion and yield improved synthesis.

The powder ratios were combined with the salt (in a 1:1 reactant to salt ratio by weight) and milled in a hardened steel bowl with mill balls (both X105CrMo17) in a Fristch Pulverisette 23 shaker ball mill in heptane. A non-polar solvent (heptane) was used to prevent any salt dissolution in absorbed water. The mill ran at 1800 oscillations per minute for 15 minutes and the resulting mixture was dried at 95 °C for 8 hours.

To better understand the morphology of the reactants, some TAC2 powder mixture was also imaged after milling without the salt. The salt's presence would have hindered interpretation of the images. Imaging was performed on a carbon adhesive stub using scanning electron microscope (SEM), a Hitachi TM3030 (15 kV). Particle sizes of the reactants were then determined from the SEM images using ImageJ (Version 1.51u, National Institute of Health) software.

To achieve MAX phase synthesis, the milled mixture of reactant and salt powder was uniaxially pressed in a single punch hand press at 140 MPa using 13 mm diameter dies. The green pellets were heated in a furnace under flowing argon (~ 0.25 L/min). The reaction took place on an alumina boat, with the pellets covered by alumina crucibles to try and reduce any salt evaporation and contamination of the furnace.

The furnace peak temperatures and dwell times at these temperatures were as follows. Different TAC2 samples were heated to a series of temperatures between 900 and 1000 °C with dwells of 2 hours. In addition to one TAC2 sample was heated to 970 °C, where it was held for 5 hours, in an attempt to further improve phase purity. The TAC3 samples were heated to 1300 °C for dwell times of 2 hours only.

The sintered pellets were then crushed by hand with a mortar and pestle and washed through a Büchner funnel with water to remove the salt. The resulting powders were then dried at 95 °C for 8 hours and analysed on a carbon adhesive stub by SEM (FEI Inspect F, 10 kV) and x-ray diffractometry (XRD) (Bruker D2 Phaser, $10^\circ \leq 2\theta \leq 70^\circ$, 0.02° step size, Cu α source). Rietveld refinements were performed using GSAS [21] and EXPGUI [22].

To determine the reaction pathway, small amounts of crushed, washed and dried powder from a selection of the individual synthesised trials were combined separately with Buehler Epoxicure 2 and poured into small sections of plastic tube within a larger mould. More Epoxicure 2 resin was carefully poured over the top and allowed to set overnight. The mounted samples were first ground (Buehler Ecomet 250 with Automet 250 head) with a P600 diamond grinding disc (Metprep Cameo Platinum series) with water lubrication, then subsequently polished with $3\mu\text{m}$ and then $1\mu\text{m}$ diamond suspensions (Metprep monocrystalline water-based) on cashmere polishing cloth (Metprep). Ultrasonic cleaning in water was then performed to remove polishing debris. The samples were carbon coated with an Agar 108CA coater, using 5V for 5s. Energy dispersive x-ray (EDX) spectra mapping, using a Hitachi TM3030 SEM (15 kV) was performed, using Bruker Quantax 70 software which was then used to determine the variation in concentration of titanium and aluminium for different areas.

3. Results

Ti₂AlC synthesis

Fig. 1 shows the XRD patterns for samples synthesised with NaCl flux at varying temperatures. The target phase is present at 900 °C, as well as ancillary sub stoichiometric TiC_{1-x} , $\text{Ti}_{0.9}\text{Al}_{1.1}$ and Ti_2Al . There is also a very weak graphite peak. As the dwell temperature is increased to 1000 °C, the abundance of the target phase grows. Increasing the dwell time to 5 hours at 970 °C also results in more Ti_2AlC at the expense of the other phases. The peaks are broad which could indicate nano-crystallinity.

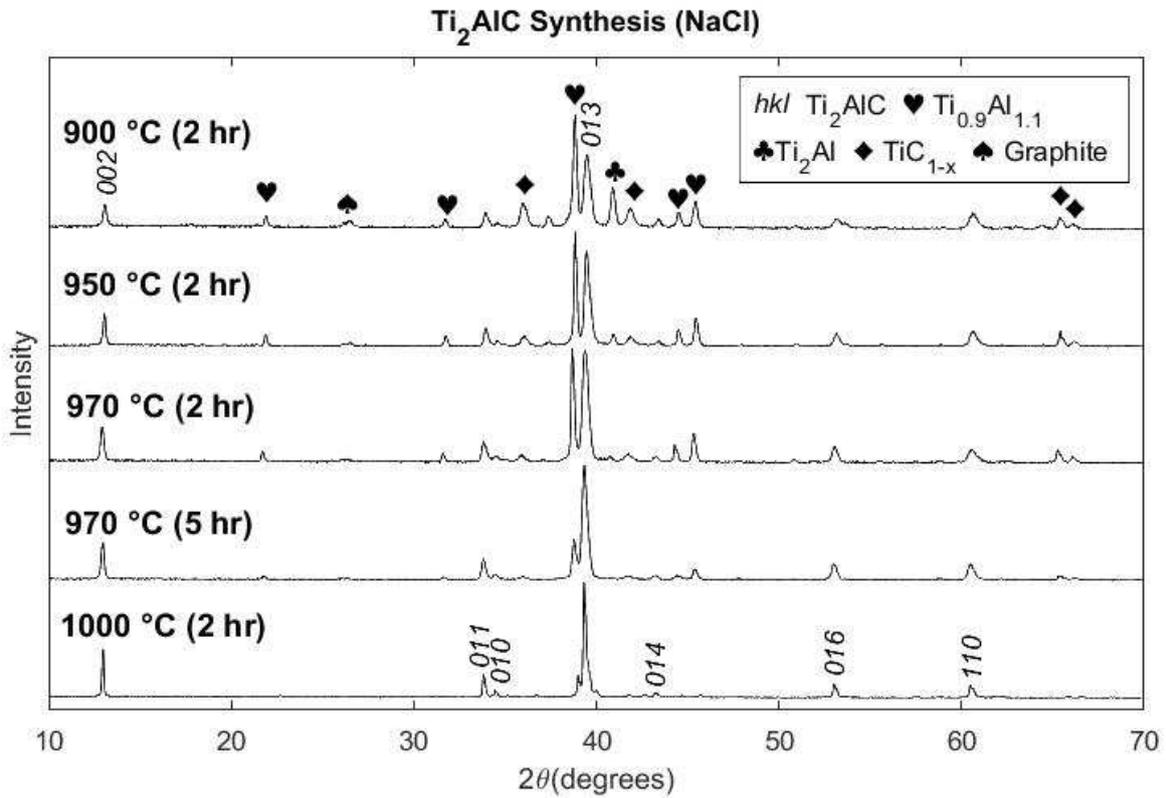


Fig. 1 –XRD patterns for TAC2 samples synthesised with NaCl under argon.

Fig. 2 compares the samples synthesised at 1000 °C using the three fluxes. Neither of the salts nor their eutectic had an appreciable effect on resulting composition other than a small graphite peak in the KCl synthesised powder. There was little difference in the composition when using the eutectic salt mix, in spite of the lower melting point.

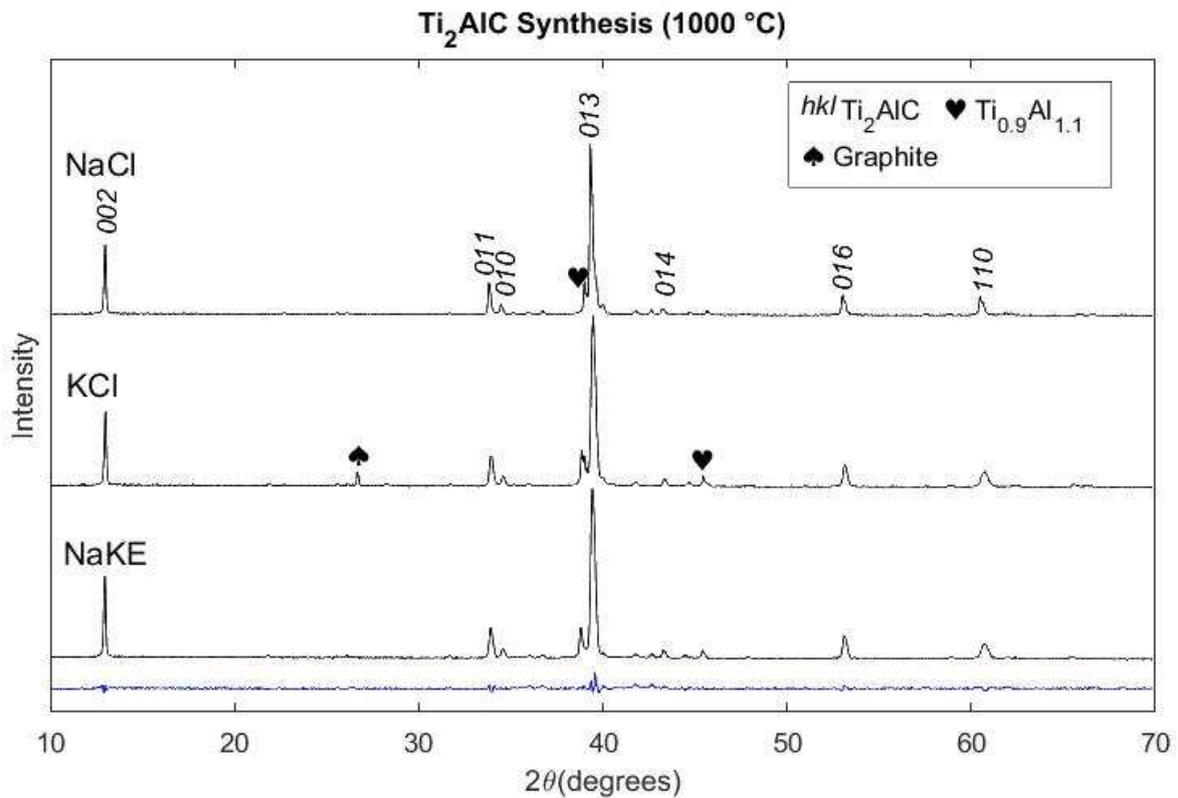


Fig.2- XRD patterns of TAC2 samples synthesised at 1000 °C with different salt fluxes. **Difference profile for Rietveld refinement of NaKE sample shown in blue.**

Rietveld refinement of the NaKE-synthesised sample at 1000 °C gives the sample composition of 88% Ti₂AlC and 12% Ti_{0.9}Al_{1.1}, with χ^2 value of 4.919 and a weighted R factor of 0.1337. Refining the structure also revealed the presence of an unknown minor phase with peaks at ~41.7 ° and 42.6 °, leading to the higher χ^2 and weighted R-factor values.

Ti₃AlC₂ synthesis

Ti₃AlC₂ was synthesised successfully at 1300 °C alongside small amounts of TiC and Ti₂AlC (Fig. 3). As with the 211 phase experiments, the choice of salt has had little effect on the product phases, but the Ti₂AlC peaks were more pronounced in the NaKE samples. As with the TAC2 samples, the peaks are broad. Rietveld refinement was performed on the NaKE-synthesised sample with QPA giving the composition by weight at 61 % Ti₃AlC₂, 21 % Ti₂AlC and 18 % TiC, with a χ^2 value of 2.603 and a weighted R-factor of 0.0997.

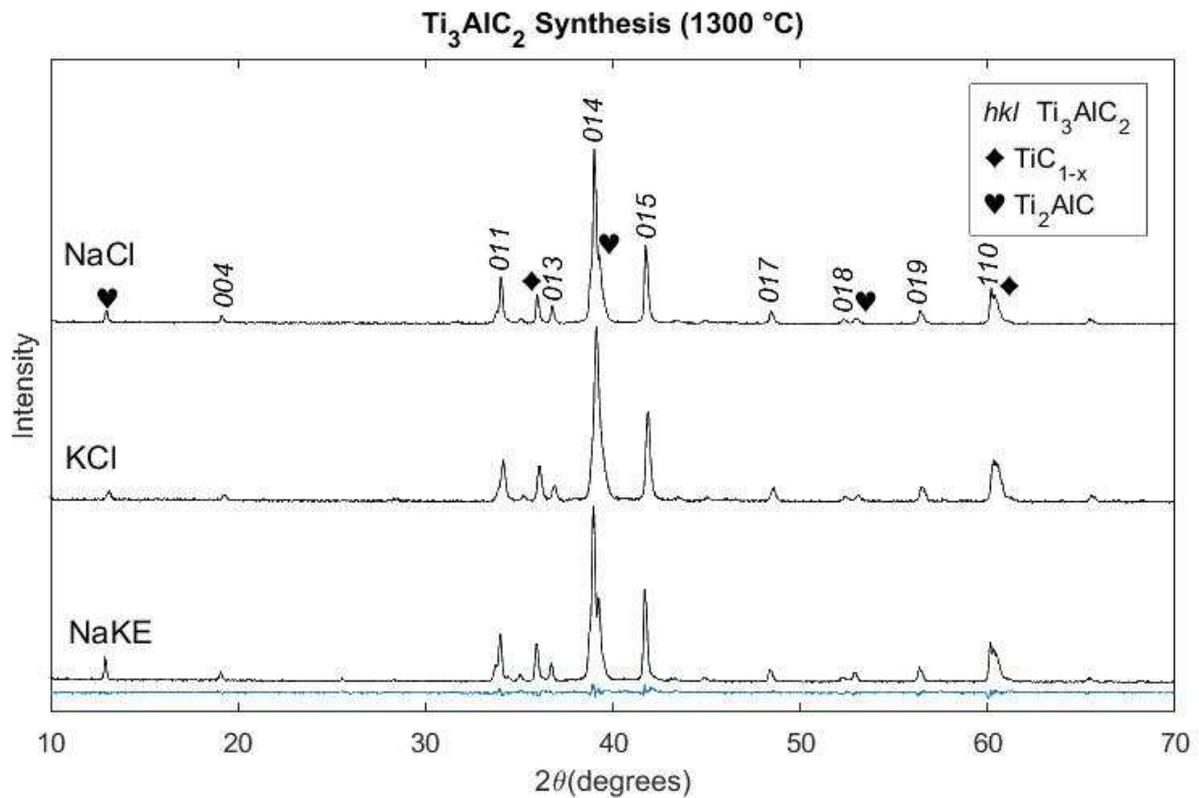


Fig.3 – XRD patterns of TAC3 samples synthesised 1300 °C for 2 hours. **Difference profile for Rietveld refinement of NaKE sample shown in blue.**

Powder morphology and reaction pathway

SEM images of TAC2 reactants milled without salt (Fig. 4) show that the precursor titanium is in smaller irregular pieces and has a mean particle size of 31 μm, while the softer aluminium has been flattened into larger flakes ~120 μm wide with small particles of titanium and graphite included as a result of milling. The graphite particles are as large as ~40 μm but have a mean size of 21 μm. As the furnace temperatures are above the melting point of aluminium, any templating from the large flakes is unlikely.

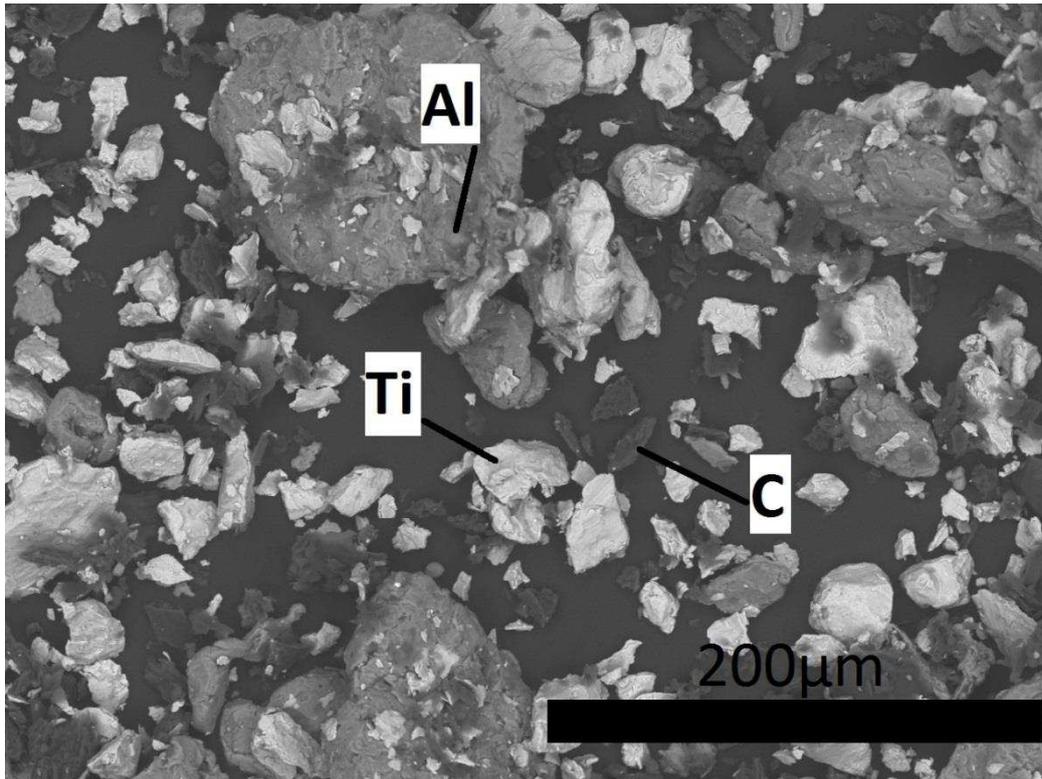


Fig. 4 Backscatter Electron (BSE) SEM Image of powder reactants.

Fig. 5 compares the morphology of 900 °C synthesised powder with that synthesised at 1000 °C. At the lower temperature, it appears that sub-micron sized particles have templated on prior micron sized particles, possibly smaller particles of titanium or aluminium from the milled powder as can be seen in Fig. 4. The morphology is inconsistent, potentially due to the presence of ancillary phases identified in the analysis shown in Fig. 2. At 1000°C, the morphology has changed substantially; the appearance is more consistent, potentially reflecting the greater phase purity (Fig. 2). In addition, the sub-micron globular grains of Ti_2AlC are clustered together in large particles, retaining less of the morphology of the reactant powders. Instead, they more closely resemble the grains of Cr_2AlC synthesised by Tian *et al.* [18].

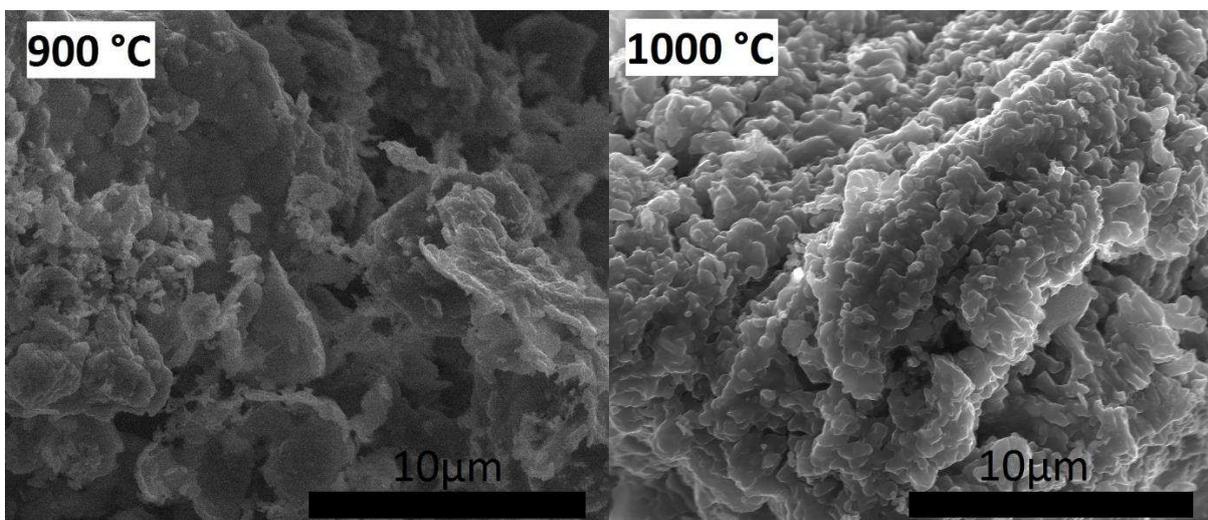


Fig. 5 – Secondary Electron (SE) SEM image of TAC2 samples after synthesis, crushing and washing.

The morphology of the Ti_3AlC_2 is shown in Fig. 6, which has needle-like grains, and is more similar in appearance to molten-salt synthesised Ti_3SiC_2 as reported by Guo *et al.* [17]. This suggests that the 312 phases are prone to forming needle shaped grains, while the 211 phases are more equiaxed when synthesised in this manner.

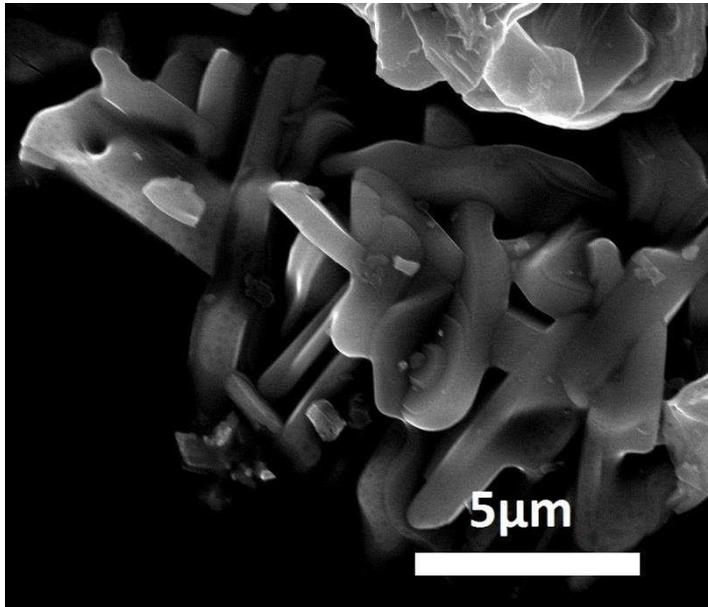


Fig. 6 – SEM image of TAC3 sample after synthesis, crushing and washing.

EDX spectra maps of mounted powders

Fig.7 shows SEM images of the mounted and polished powders synthesised at 900°C and 1000 °C in KCl. Among smaller pieces, there are large ‘rings’ visible with dark centres. From this it is seems apparent that templating has occurred on larger particles of graphite, but they may also be voids left by salt dissolution, which have been subsequently filled with resin. Due to the carbon coating procedure and the carbon-based nature of the resin, the EDX carbon signal was unable to determine the answer. EDX spectra maps in Fig.7 of the 900 °C sample show a ring of titanium immediately around the dark region, with aluminium and titanium towards the particle surface. There are also regions of higher aluminium content than titanium. This inner ring corresponds to TiC , which gives way to titanium aluminides towards the outer edges of the particle. The high aluminium signal regions at the periphery of the image correspond to $TiAl_2$. The sample synthesised at 1000 °C is far more uniform and shows no hidden voids or graphite ‘seeds’, confirming the reaction pathway as TiC forming on graphite, and $TiAl$ forming from liquid aluminium and solid flakes of titanium.

To determine whether the dark region in the 900 °C sample was a graphite particle or a void filled with resin, the carbon coating was removed by polishing and the sample was examined with Raman spectroscopy (InVia Raman Microscope, 10x 10s acquisitions, using a 625 nm 20 mW argon laser). Inset in Fig. 7 shows the Raman spectral analysis for both a region of resin and the centre of a black region with a ‘ring’ similar to the one shown in the SEM image. Comparing the spectra reveals that the resin acquisition is very different to the centre of a ‘ring’ which seems to suggest that the rings are templated material on a graphite flake. The large peak on is at $1350cm^{-1}$ which corresponds to the D band for graphite [23].

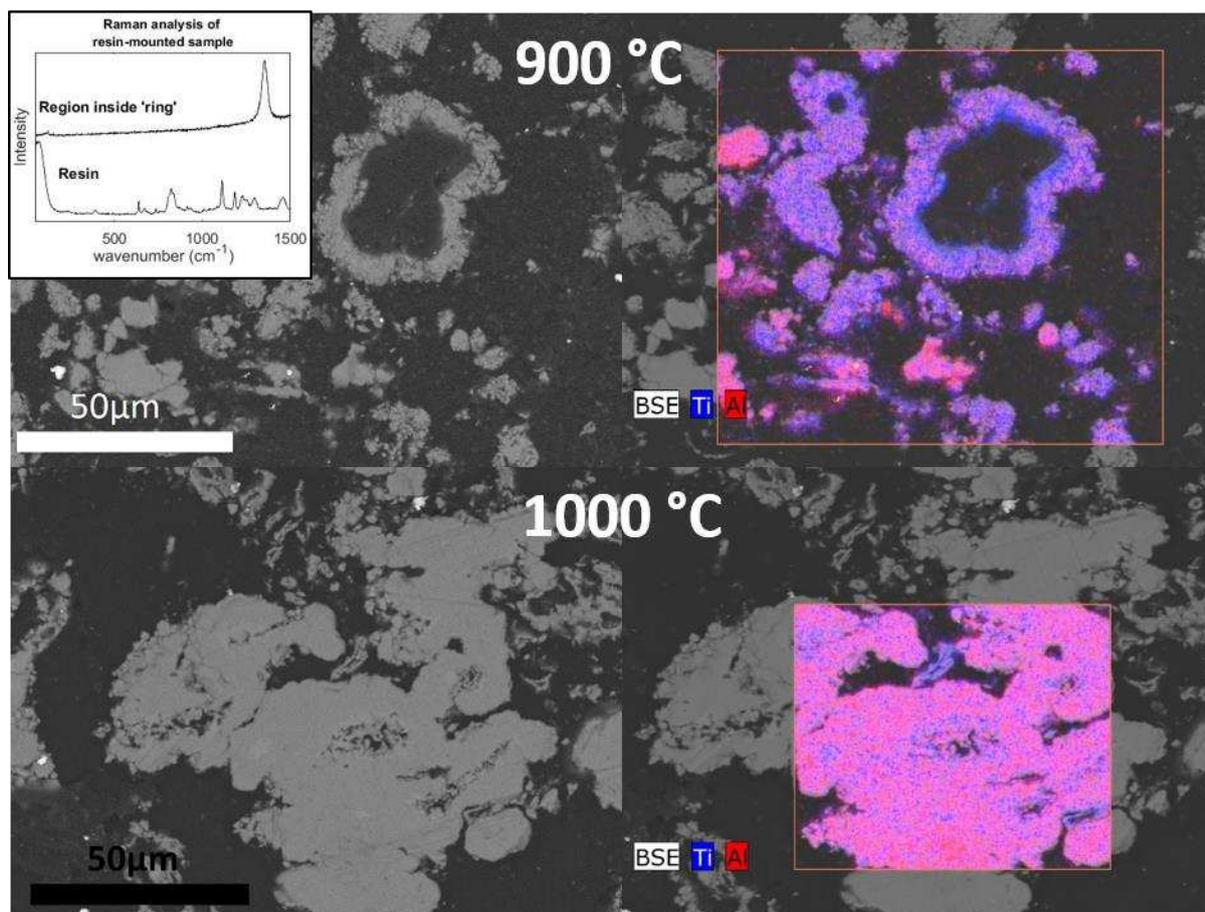


Fig. 7 – BSE SEM images and EDX maps of TAC2 samples synthesised at 900 °C (top) and 1000 °C (bottom). Raman analysis of dark region inside ‘ring’ and empty resin (top, inset).

4. Discussion

The proposed reaction pathway for TAC2 samples is that TiC forms along with TiAl intermetallic, when the salt and aluminium melt, which then react to form Ti_2AlC . The pellets largely retained their shape and structure after being heated in the furnace, which indicates large scale dissolution of the reactants in the salt did not occur, therefore templating is more likely. From the resin mounted SEM cross sections, the TiC templates on flakes of graphite, forming a shell. At higher temperatures these graphite ‘seeds’ disappear as the reactants convert to Ti_2AlC . The D band peak noted in the Raman spectra of the graphite is usually forbidden, indicating some disorder which is consistent with ball milling [23]. This reaction pathway is in agreement with reaction pathways for Ti_2AlC synthesis through other methods in the literature [9] [24] [25].

The TAC3 samples had ancillary TiC and Ti_2AlC peaks, the latter of which are more intense in the NaKE synthesised sample, possibly due to the lower melting temperature of the salt eutectic. At 1300°C a large quantity of the salt evaporated and coated the inside of the crucibles, perhaps explaining why the product is not as pure.

5. Conclusion

Ti_2AlC and Ti_3AlC_2 powders were successfully synthesised from elemental powders using molten salt as a flux to aid the reaction. Ti_2AlC was present at 900°C but required ~970°C and a dwell of 5 hours

to increase concentration. After 1000 °C synthesis, the sample made with NaCl and KCl contained 88% Ti₂AlC. Ti₃AlC₂ was synthesised successfully at 1300°C alongside Ti₂AlC. In both cases, the choice of salt had little bearing on the production of the target phases. The morphology of the 211 phase appears more globular than the long needles of Ti₃AlC₂. The growth of Ti₂AlC begins with TiC_{1-x} growth on graphite flakes and formation of titanium aluminides, which then combine to form Ti₂AlC. Increasing the temperature and changing the stoichiometry encourages the growth of Ti₃AlC₂ over Ti₂AlC.

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