Structural, Physical and Mechanical Properties of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ Solid

Solution with $x=0-1$

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Abstract

A series of high-purity $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions with $0 < x < 1$ were reaction sintered from Ti, Si, Al and TiC powders using Pulsed Electric Current Sintering (PECS)¹. The a-lattice parameter of all sintered solid solutions remains constant at approximately 0.307 nm, while the c-lattice parameter decreases from 1.858 nm to 1.763 nm with increasing amount of Si. The specific heat capacity of $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$ was found to be comparable to that of end-member MAX phases, namely Ti_3AlC_2 and Ti_3SiC_2 , while its coefficient of thermal expansion (CTE) was lower than that of the end members. Both Young's and shear moduli increase with increasing amount of Si. Vickers hardness (H_V) measurements demonstrate significant hardening effect in $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions regardless of the grain size, i.e. it changes from 4.1 ± 0.14 GPa of Ti_3AlC_2 and 4.2 ± 0.37 GPa of Ti_3SiC_2 , up to 5.6 ± 0.2 GPa for $\text{Ti}_3(\text{Al}_{0.4}\text{Si}_{0.6})\text{C}_2$. At room temperature, the strengthening effect was found to be marginal in the fine grained structure, as

¹This method is commonly but inaccurately referred to as Spark Plasma Sintering (SPS).

the compressive strength of $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$ and $\text{Ti}_3\text{Al}_{0.4}\text{Si}_{0.6}\text{C}_2$ is higher for only 7.6% when compared to that of the end members. However, significant strengthening effect was observed in coarse grained structures as the room temperature compressive strength of solid solutions exceed those of two end-members for more than 30%. Nevertheless, above brittle-to-plastic transition temperature, the solid solution strengthening effect diminishes and the strength of Ti_3SiC_2 is significantly higher than that of Ti_3AlC_2 and solid solutions. Finally, it was found that $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$ forms protective alumina oxide layer at 1200°C , rather than silica that is commonly found on oxidized surfaces of Ti_3SiC_2 .

1 Introduction

The MAX phases are the family of more than 70 ternary carbides or nitrides with layered nanolaminated structure having $P6_3/mmc$ hexagonal crystal structure and common chemical formula $\text{M}_{n+1}\text{AX}_n$, where M is transition metal, A is A-group element, X is carbon or nitrogen, and $n=1-3$ [1-3]. The MAX phases are sometimes referred to as "metallic ceramic" since they possess a unique combination of properties that place them in the middle ground between typical ceramics and metals [3, 4]. On one hand, MAX phases, like other typical ceramics, have high stiffness, good chemical and oxidation resistances, high hardness, low coefficient of thermal expansion and good thermodynamic stability up to high temperatures [3]. However, they have high thermal and electrical conductivity, good thermal shock resistance and can be even easily machined like typical metals [2-6]. Their properties are even more remarkable when one considers that they can be compressed to stresses over 1 GPa, showing fully reproducible stress-strain hysteresis loops while dissipating 25% of the mechanical energy [7, 8]. At higher temperatures, however, MAX phases undergo a brittle-to-plastic transition (BPT) [9] and can be

plastically deformed for more than 25% before failure even under tension [7-9]. Finally, they can be fabricated inexpensively using a variety of reaction sintering methods [3].

Numerous studies suggested in the past that substitution on M, A, or X site in $M_{n+1}AX_n$ can improve physical, chemical and mechanical properties of the MAX phases. Thus, MAX phase solid-solutions hold potential for tailoring properties of this class of materials for different applications[10-17] by substitution (alloying) on M, A and/or X sites[5]. The elements used for substitution are generally neighboring elements in the periodic table of elements with similar atomic radii and electronic structure. Until now, approximately 100 different solid solutions have been fabricated and characterized. Some examples of the most studied ones include $(Cr_{1-x}V_x)_2AlC$ [18], $(Ti,Nb)_2AlC$ [19], $Cr_2(Al_{1-x}Si_x)C$ [20], $(Ti_{0.5}V_{0.5})_3AlC_2$ [14], $Ti_3(Al_{0.75}Si_{0.25})C_2$ [21-23], $Ti_3Al_xSn_{1-x}C_2$ [24], $Ti_3Ge_xSi_{1-x}C_2$ [25, 26], $Ti_2Al(C_{0.5}N_{0.5})$ [27, 28] and $Ti_3Al(C_{0.5}N_{0.5})_2$ [29]. A number of theoretical studies has also addressed phase stability, electronic, elastic, thermal and optical properties of different MAX phase solid solutions [30-33]. Most recently, we have shown, using cluster expansion method, that the number $(M_x,M'_{1-x})_2AX$ phase solid solutions can be significantly extended even to those compositions having M' alloying elements that otherwise does not form an end-member MAX phase [34]. Previous studies also showed that while some solid solutions such as $Ti_3(Al_{0.75}Si_{0.25})C_2$ [21-23], $Ti_3Al_xSn_{1-x}C_2$ [24, 35] and $Ti_2Al(C_{0.5}N_{0.5})$ [27, 28] show improved mechanical properties due to solid solution hardening effect, the others, such as $Cr_2(Al_{1-x}Si_x)C$ [20], $Ti_3Ge_xSi_{1-x}C_2$ [25, 26], $(Ti,Nb)_2AlC$ [19, 36], show the opposite effect, i.e. solid solution softening. The reason for observed hardening effect in some MAX phase solid solutions, and softening in the others, are not completely clear at this moment [23, 24, 26, 37].

Because Ti_3SiC_2 and Ti_3AlC_2 are the most studied and the best characterized members of MAX phases, it is not surprising that $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ were among the first MAX phases solid solutions investigated in the past [23, 31, 38-40]. $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions are expected to have a good combination of properties that are important for their application as a high-temperature structural materials. It is suggested that $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions could provide good oxidation resistance like Ti_3AlC_2 due to formation of the pure alumina protective oxide layer [39, 40] and better high-temperature mechanical properties like Ti_3SiC_2 . However, Lee et al. and Nguyen et al. showed that oxidation of $\text{Ti}_3(\text{Al}_{0.5}\text{Si}_{0.5})\text{C}_2$ and $\text{Ti}_3(\text{Al}_{0.7}\text{Si}_{0.3})\text{C}_2$ in the 900-1200°C temperature range results in formation of the mixed oxide layer consisting of rutile- TiO_2 , Al_2O_3 , and amorphous SiO_2 [40, 41]. Correspondingly, like in the case of other MAX phases solid solutions, there is no strong agreement on the solid solution hardening and strengthening effects in $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$. For example, Zhou et al. demonstrated that as x increases from 0 to 0.25 in $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$, the Vickers hardness and room temperature compressive strength increased for up to 26% and 29%, respectively [23]. In addition, first principle studies by Son et al. [30] also showed significant hardening effect in $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solution due to chemical hardening caused by strong Si-Al interactions in A layer. However, another study indicated no hardening effect as the Vickers hardness decreases linearly from Ti_3SiC_2 to Ti_3AlC_2 [31]. It is worth noting here that all previous experimental and theoretical studies on $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ agree that lattice parameters and elastic moduli of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions lie in between the two end members [31-33].

In this study, a series of high-purity $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0) were reaction sintered from Ti, Al, Si, and TiC powder mixtures. A systematic experimental study of structure, lattice parameters, thermal expansion coefficients, heat capacities and elastic properties

are carried out to determine the effects of Si amount in $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions on their structural, physical and mechanical properties. In addition, hardening and strengthening effects in $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ are studied and discussed in more detail. Finally, oxidation of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions at 1200°C is compared to that of the end-members.

2 Experimental details

Commercial Ti (44 μm average particle size, 99.5% purity), Si (44 μm average particle size, 99.5% purity), Al (44 μm average particle size, 99.5% purity) and TiC powders (2–3 μm average particle size, 99.5% purity), all from Alfa Aesar, MA, USA, were used as starting raw materials to synthesize $\text{Ti}_2(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ MAX phase solid solutions, with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 , respectively. A series of different powder mixtures were reaction sintered using pulsed electric current sintering (PECS)². The nominal composition (Ti:Al:Ti:C ratio) of the powder mixtures and sintering conditions in Table 1 were optimized to fabricate the bulk samples with the smallest amount of impurities (second phases) and comparable grain sizes. The powder mixtures were mixed homogeneously by ball-milling in a glass jar, using zirconia beads for 24 hrs at a speed of 300 rpm. Ball-milled powder mixtures were poured into a cylindrical graphite die with an inner diameter of 20 mm and reaction sintered using PECS in the 1500–1600 $^\circ\text{C}$ temperature range with a heating rate of $50^\circ\text{C}/\text{min}$, and the holding time of 15 min. Before heating, the PECS chamber was evacuated to 10^{-6} torr and after that sintering was carried out under constant flow of ultra-high purity argon (99.999%). A constant loading of 50 MPa was applied throughout the sintering process while the cooling rate was $200^\circ\text{C}/\text{min}$. The density and relative density of sintered $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions were determined to ASTM

²This method is commonly but inaccurately referred to as Spark Plasma Sintering (SPS).

C20-00 standard using alcohol immersion Archimedes' method described in more detail elsewhere [8, 42].

The surfaces of all reaction sintered samples were polished to characterize their microstructure and composition. The phase identification of samples sintered at different temperatures was conducted using X-ray diffraction (Mode D8 Advance, Bruker AXS, Madison, WI) with Cu_α radiation, at a rate of 0.015s/step and a step time of 0.2s. The microstructure of all samples and fracture surfaces after mechanical testing were characterized using a field emission scanning electron microscope (FE-SEM; Quanta 600 FEG, FEI, Oregon) equipped with energy dispersion spectrometer (EDS). The later was used to analyze chemical composition of the phases. The surfaces of samples were prepared for FE-SEM microstructural analysis by grinding them with SiC sand paper (up to 1000grit) and polishing with diamond suspension (up to 1 μm). To expose the grains and determine the grain size, the polished surfaces were also etched for 10-15 seconds using a solution of $2\text{H}_2\text{O}:1\text{HNO}_3:1\text{HF}$. The grain size of more than 50 grains in each sample was measured from SEM images using the ImageJ software.

The specific heat capacity at the constant pressure were determined from differential scanning calorimetry (DSC Q 20, TA Instrument, New Castle, DE) results obtained in the -50°C and 300°C temperature range, following the procedure described in ASTM E 1269 standard. All tests were carried out under dry nitrogen at the flow rate of 50ml/min. Each sample was heated and cooled twice with the rate of 10°C /min and dwelling time of 4minutes at -50°C and 300°C. Prior to the testing, the heat flows of an empty alumina specimen holder and a synthetic sapphire standard (TA Instruments, New Castle, DE) were also separately measured. Then, the specific heat capacity of $\text{Ti}_2(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ was calculated as $C_{sp} = C_{st} \cdot \frac{D_{sp} \cdot W_{st}}{D_{st} \cdot W_{sp}}$ where, C_{sp} and C_{st} are the specific heat capacity of the $\text{Ti}_2(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ specimens and sapphire standard, respectively.

D_{sp} and D_{st} indicate the vertical displacement between the sample or sapphire standard and the empty specimen holder, and W_{st} and W_{sp} represent the weights of sapphire standard and sample, respectively.

Coefficients of thermal expansion (CTEs) of solid solutions and end members were determined using Thermo-mechanical Analyzer (TMA Q 400, TA Instrument, New Castle, DE) according to ASTM E 831 standard. All specimens were EDM-machined into disks with diameter of 5mm and thickness of 8mm. A constant load of 0.1 N was applied through the probe to ensure a perfect contact between the probe and sample surfaces. All samples were tested in two heating-cooling cycles at a rate of 5°C/min between 25°C and 600°C, and a dwelling time of 5 minutes at the initial and final temperatures. The instantaneous coefficient of thermal expansion (α) was calculated from as: $\alpha = \frac{\Delta L * k}{L * \Delta T}$, where ΔL is the change of specimen length, ΔT is the temperature difference over which the change in specimen length was measured and k is calibration coefficient.

Elastic modulus were determined at room temperature using Resonant Ultrasound Spectroscopy (RUS, Magnaflux Quasar Systems, NM) following procedures described in more detail elsewhere [21, 42, 43]. All RUS samples were machined into parallelepipeds with sharp edges and a parallelism within 1%. The samples were supported by three sapphire transducers - one transmitting a sinusoidal continuous-wave signal with a constant amplitude but varying frequencies in the range of 0 to 400 kHz and the other two ones detecting the oscillation response directly from the sample. Young's and shear moduli were determined from the corresponding resonance spectrum for the sample of known weight, geometry and dimensions using Quasar RuSpec software (Magnaflux Quasar Systems, NM). Quasar RuSpec software was able to iteratively minimize error between the measured and calculated resonant peaks by changing the

c_{11} and c_{44} constants until the acceptable error ($<0.3\%$) between measured and calculated frequencies of resonance peaks was obtained.

The Vickers hardness of all samples was determined using Micro-hardness Tester LM 300AT (LECO, MI) at indentation loads of 5N and 10N. Vickers hardness was calculated as $H=2P/d^2$, where P is indentation load, d is the average length of indent's diagonals. At least twenty measurements were carried out at each indentation load, the data reported here are the statistic average of those measurements.

The ultimate compressive strength of samples was determined using 810 Materials Testing System (MTS 810, MN) at different temperatures ranging from the room temperature to 1100 °C. Cylindrical specimens with a diameter of 5mm and height of 8mm were machined from the center of reaction sintered discs using electron-discharge-machining. Both flat surfaces on the specimens were gently grinded to shape edge and to obtain parallelism with 1% using 1000 grit sand papers. The sample was sandwiched between two SiC spacers and a high precision, high temperature extensometer (632.59E-77, MTS, USA) was attached to the spacers to record the strain. The uniaxial compressive tests were carried out under the displacement control mode with a strain rate of 10^{-4} s.

3 Results and Discussion

3.1 Structural characterization of $Ti_3(Al_{1-x}Si_x)C_2$ solid solutions

A series of reaction sintering experiments, followed by XRD analysis were carried out to optimize nominal composition of powder mixtures and sintering conditions and ultimately fabricate XRD phase-pure samples of $Ti_3(Al_{1-x}Si_x)C_2$ with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 . Since melting points of Al (660 °C) and Si (1414 °C) and their evaporation rates are different in different sintering conditions, Ti:Al:Si:C ratio in the initial powder mixtures and sintering

conditions has to be carefully adjusted to obtain XRD phase pure $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ with the minimal amount of secondary phases (mostly TiAlSi intermetallics and TiC). Secondary phases in the MAX phases sintered from elemental powders could be: (i) in thermodynamic equilibrium with the MAX phase if final chemistry of the product deviates from the targeted stoichiometry; or (ii) result of incomplete reaction during sintering. In addition, PCES in graphite die creates carbon rich environment during sintering, and thus amount of carbon in the initial powdered mixtures was adjusted to substoichiometric to avoid formation of TiC . The optimized nominal compositions of the initial powders and sintering conditions are summarized in Table 1. As it can be seen in Table 1, the sintering temperature has to be gradually elevated from 1510°C for Ti_3AlC_2 to 1600°C for Ti_3SiC_2 with increasing Si content in solid solutions to promote liquid assisted reaction sintering. In addition, about 10-20% of extra Al and Si was added to initial powder mixture to compensate their evaporation during sintering process and amount of the molten metal and intermetallic compounds that squeezes out through the gaps between punch and die during initial stages of sintering process [44-46].

Figure 1 shows the XRD patterns of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ MAX phase solid solutions obtained using optimized nominal compositions of initial powders and sintering condition in Table 1. XRD results in Figure 1 show that all sintered samples are pure and contain mainly $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ MAX phase. However, a small amount of TiC phase was present in samples for $x > 0.4$. Further analysis of XRD patterns indicated that amount of TiC was always below 3.6 wt%. Figure 1 also shows a shift of some XRD peaks with increasing Si content; the most obvious one is that of (002) peak which shifts from 9.3° to 9.9° with increasing Si content.

The a- and c- lattice parameters retrieved from XRD patterns using Jade software (Materials Date, Livermore, CA) are plotted in Figure 2 as a function of x in $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$.

$\text{Ti}_{1-x}\text{Si}_x\text{C}_2$. Figure 2 shows no changes in the a-lattice parameter with increasing Si content (Ti_3AlC_2 : 0.3072nm; Ti_3SiC_2 : 0.3065nm). However, the c-lattice parameter decreased linearly from 1.86nm to 1.78nm with increasing amount of Si in solid solutions. The lattice parameters of Ti_3AlC_2 and Ti_3SiC_2 reported here (Ti_3AlC_2 : a=0.3072nm, c=1.854nm; Ti_3SiC_2 : a=0.3065 nm, c=1.767nm) are in good agreement with previously reported experimental values (Ti_3AlC_2 : a=0.3073nm, c=1.858nm [47]; Ti_3SiC_2 : a=0.3066 nm, c=1.763nm [48]). However, although the experimental values of a- and c- lattice parameters reported here for solid solutions are slightly below those obtained in previous *ab initio* calculations [30, 32] in Figure 2, their changes with Si content follow the same trend as predicted in those studies. Son et al. [30] suggested that the observed trend can be explained to be result of the charge density of A element and consequently stronger ionic and covalent character of M-A bonds with increasing Si content on the A sites.

A selected , but typical SEM image of $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ obtained in the back scattered mode is shown in Figure 3, together with Ti, Al and Si EDS elemental maps. Although the XRD results in Figure 1 show no presence of other phases but $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$, Figure 3 suggests (see darker gray phases in Figure 3-a) that sample contains a small amount of secondary phases. Analysis of SEM back-scattered images and EDS results for all sintered samples (not shown here) revealed that main secondary phases were TiC, TiSi_x and/or TiAl_x intermetallics, and that their total amount was very small, i.e. always below 5%. Therefore, it is not surprising some of them could not be detected in XRD patterns as their amount was very small.

Surfaces polished for SEM were further etched to expose grains and measure their length and width, and those results are summarized in Figure 4. All as-sintered fine grained (FG) $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions have similar grain size, i.e. around 6.6 μm in length and 2.2 μm in width, except $\text{Ti}_3\text{Al}_{0.8}\text{Si}_{0.2}\text{C}_2$. In the case of $\text{Ti}_3\text{Al}_{0.8}\text{Si}_{0.2}\text{C}_2$, the grains were $12.7 \pm 8.8 \mu\text{m}$ long and

3.7±1.3 μm wide due to the promoted grain growth at higher sintering temperature ~1550 °C. Numerous attempts to optimize sintering conditions and fabricate Ti₃Al_{0.8}Si_{0.2}C₂ samples with high purity but grain size of approximately 7 x 3 μm were unsuccessful for the reasons that are not clear at this moment. In addition, selected Ti₃(Al_{1-x}Si_x)C₂ samples were also heat-treated to promote grain growth and make samples with the larger grain sizes for mechanical testing. The heat-treatment conditions and the grain size distribution for coarse grained (CG) samples are also listed in Table 2 and summarized in Figure 4-b, respectively. After heat-treatment, grains in all heat treated samples were measured to be around 25 μm in length and 8 μm in width.

The density and relative density of Ti₃(Al_{1-x}Si_x)C₂ samples increases from 4.17g/cm³ to 4.51g/cm³ with increasing amount of Si in solid solutions, Figure 5. Reported theoretical densities of 4.25g/cm³ for Ti₃AlC₂[47] and 4.53 g/cm³ for Ti₃SiC₂[47] are in good agreement with our experiment results and show that the relative densities of all processed samples are above 97%. Thus, results presented here indicate that PECS is a powerful tool to reaction sinter not only XRD pure, but also almost fully densified MAX phase solid solution in a short time (less than 15 minutes per sample) and at relatively lower temperatures.

3.2 Thermal properties of Ti₃(Al_{1-x}Si_x)C₂ solid solutions

The heat flow measured using DSC and calculated specific heat capacity at constant pressure (c_p) are plotted in Figure 6 as a function of temperature for Ti₃(Al_{0.6}Si_{0.4})C₂ solid solution and its end-members. The results in Figure 6 show that heat capacity of the solid solution and two end members are almost identical, and in all cases it increase monotonically with increasing temperature from 0.5 J/(g·K) at -50°C to 0.7 J/(g·K) at 300°C.

Coefficients of thermal expansion (CTE) at room temperatures were determined from TMA results to be $7.54 \times 10^{-6} \pm 0.5 \text{ K}^{-1}$, $7.66 \times 10^{-6} \pm 0.46 \text{ K}^{-1}$ and $7.88 \times 10^{-6} \pm 0.59 \text{ K}^{-1}$ at

the room temperature for $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$, Ti_3AlC_2 and Ti_3SiC_2 , respectively, and they increase gradually with temperature, Figure 7. The previously reported average CTEs of $\sim 9.1\text{--}9.2 \times 10^{-6} \text{ K}^{-1}$ [48] for Ti_3SiC_2 and $9.2 \times 10^{-6} \text{ K}^{-1}$ for Ti_3AlC_2 [48], are slightly higher than those obtained in this study, and closer to the values obtained at 300°C in this study. Figure 7 also shows that CTEs of solid solution are lower than those of end members at all temperatures. The latter is in good agreement with the first principle calculations [38] showing that an additional valence electron from Si occupies more stable and stronger Ti d–Si p and Ti d–Al p covalent bonding states thus strengthening a weak inter-planar cohesion between Ti and Al(Si) atomic planes. Therefore the CTE value of solid solutions would decrease slightly when compared to two end members most likely due to stronger Si–Al interactions/bonding in solid solution, than Si–Si or Al–Al in end members.

3.3 Elastic moduli of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions

Figure 8a shows changes of the room temperature Young's (E) and shear (G) moduli with Si content as determined by Resonant Ultrasound spectroscopy (RUS). E increases linearly from 300 GPa for Ti_3AlC_2 to 325 GPa for Ti_3SiC_2 with increasing amount of Si on the A site, which is in good agreement with modeling results reported by Son et al [30] and Zeng et al. [32]. Shear modulus was also found to increase linearly from 128 GPa to 140 GPa with increasing amount of Si on the A sub-lattice. Results of previous Density Functional Theory also suggested that the observed increase in the elastic moduli with increasing amount of Si on A sub-lattice can be explained by charge density increase near the A element and stronger M–A bonding [30, 32].

However, at high temperature, E decreased slightly with increasing temperature for all solid solutions and end-members as it is illustrated in Figure 8b, without showing any deviation from the monotonic decreasing trend at BPT temperature around 900°C . Comparison with DFT calculation for two end members [49] in Figure 8 shows that experimental and modeling results

are in relatively good agreement, with slightly smaller decrease of predicted elastic with increasing temperature.

3.4 Vickers Hardness of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions

The Vickers hardness of as-sintered FG and CG samples obtained using indentation loads of 5N and 10N are plotted in Figure 9-a as a function of Si content. Vickers hardness increases from 4.2GPa for Ti_3AlC_2 at the load of 10N, then it reaches value of 5.2GPa for $\text{Ti}_3\text{Al}_{0.4}\text{Si}_{0.6}\text{C}_2$, and at in the end, it decreases again to 4.3GPa for Ti_3SiC_2 . As it can be also seen in Figure 9-a, both FG- and CG- $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions have almost identical hardness values at all compositions. From the results in Figure 9-a the maximum hardness can be located at composition of around $x=0.5$ at both indentation loads of 5N and 10N, suggesting ideal solid solution hardening behavior.

Figure 9-b shows selected but typical the SEM image of the indentation after Vickers testing. As it is typical for all MAX phases, a significant deformation by kinking and delamination can be observed around the indent (Figure 9-b)[50], instead of corner cracks that usually form during indentation in a typical brittle ceramics. This unusual behavior of MAX phases is attributed to the fact that they deform by easy dislocation glide in the basal planes, and by grain backing and kink bend formation during indentation testing [50]. The later, together with the fact that Vickers hardness shows maximum values at $x=0.5$, suggests that substitution of Al with Si on the A sub-lattice affects dislocation dynamics and results in the ideal solid solution hardening. According to Density Functional Theory calculations, the changes of the calculated hardness values derived from the cleavage energy between M and A layer for the cleavage along the basal plane with Si content (Figure 9-a) also suggests a solid solution hardening behavior in $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ system[30]. However, the hardness derived from the cleavage energy cleavage

higher than that reported here because Vickers hardness measurements involves several grain with different orientation relative to loading directions and more complex stress distribution under indent, when compared to the case of the pure cleavage in basal plane [33]. Nevertheless, the experimental Vickers hardness and the modeling results share the similar trend showing ideal solid solution hardening behavior with highest harnesses at $x \sim 0.5$.

3.5 Mechanical properties of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ compression

The average compressive strengths of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions and its end members determined from 3 or 4 tests are plotted in Figure 10, as a function of Si content and grain size. For comparison, compressive strengths of end members reported before are also plotted in the same figure [44, 47, 51-53]. As it has been already very well established in the case of other MAX phases [54, 55], compressive strength of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions is a strong function of grain size, with FG samples showing significantly higher compressive strength than the CG ones in Figure 10. Results in Figure 10 also show very mild solid strengthening effect in FG samples, with the maximum strength for FG- $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ that is only 7.3% or 8.8 % higher than that of end-members. However, Figure 10 also indicates that compressive strength of CG samples is a strong function of Si content as the strengths of CG- $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ and $\text{Ti}_3(\text{Al}_{0.4}\text{Si}_{0.6})\text{C}_2$ solid solutions are improved for more than 30% relative to the end members. Figure 11 shows selected but typical photographs of samples after testing in compression and FE-SEM images of fracture surfaces for FG and CG samples. While FG samples shattered in the large number of pieces at the maximum compressive stresses, like typical brittle ceramics, the CG samples show more graceful failure as they fractured by propagation of the major crack in the direction of maximum shear. The SEM images of fracture surfaces in Figure 11 also reveal predominantly brittle failure by delamination in FG samples with very little kinking and grain

pull-outs, while significant deformation of individual grains by kinking can be observed on SEM images of fracture surfaces in CG structures.

When results presented here are put in conjecture with the previous results reporting on the effect of grain size on mechanical properties of MAX phases [2, 51, 55], one can conclude that solid solution can be effectively used to strengthen MAX phases only if they have relatively coarse grained structure. As it was discussed by Benitez et al. [54], very fine grained MAX phases behave more like a typical brittle solids in compression since (i) bucking and kinking of individual grains is difficult, if not impossible; and (ii) they contain more grain boundaries that are effective barriers for dislocation glide in basal planes. Therefore, only moderate effect of solid solution strengthening can be observed in FG structures by alloying on the A site. However, as deformation of individual grains by dislocation glide in basal planes and formation of low angle kink boundaries (i.e. dislocation walls) is much easier in CG structures [54], we can observe a stronger solid solutions strengthening effect. The importance of this finding cannot be overemphasized, as it implies that one has to test and compare strength of samples with the same grain sizes but different composition to make valid conclusion on the solid solution strengthening in the particular MAX solid solutions system.

Figure 12 shows typical stress-strain curves of high-purity FG $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions obtained in compression in 25°C – 1100°C temperature range. All samples show the BPT between 700°C and 900°C, below which they fail in the brittle manner. Above BPT, they failed gracefully with large strains to failure. Note here that all stress strain curves above BPT show maximum stress value at engineering strains of approximately 3%. At engineering strains exceeding ~3%, engineering stress measured in the end-members decreases and reaches almost constant value with increasing strain, i.e. they creep, before they finally fails. However,

$\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ shows qualitatively different behavior with apparent hardening (or increase in engineering stress) at engineering strains exceeding $\sim 7.5\%$ and $\sim 12\%$ at 1000°C and 1100°C , respectively. Although this apparent hardening can be considered as the manifestation of solid solution effect on the dislocation dynamics, it can be also an experimental artifact since the engineering stresses reported here do not take into account significant barreling of the samples, i.e. significant changes in their cross section area during testing above BPT temperature.

Therefore, in the remainder of this section, we compared only maximum values of the stresses at below engineering strains of 5% .

To further analyze mechanical behavior $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions, the average ultimate compressive strengths (below engineering strain of 5%) and strains to failure were plotted as a function of temperature for $x=0, 0.4$ and 1 in Figure 13. Figure 13-a clearly demonstrates that below 700°C , FG Ti_3AlC_2 and Ti_3SiC_2 with the almost identical grain sizes also have almost identical compressive strength, while $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$ solid solution with the same grain size shows slightly higher strain to failure ($\sim 7\text{-}8\%$ up 500°C) when compared to the end members. More importantly, Figure 13-b shows that:

- (i) Compression strength of Al-containing MAX phases, namely Ti_3AlC_2 and $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$, decrease more rapidly above BPT with increasing temperature when compared to Ti_3SiC_2 ;
- (ii) Solid solution strengthening completely diminishes above BPT temperature, although compressive strength of $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$ solid solution is still higher than that of Ti_3AlC_2 at 1100°C for $\sim 17.5\%$, and but far below that of Ti_3SiC_2 ;
- (iii) Decrease in compressive strength with temperature at around BPT temperature is more gradual in the solid solution than in the end members.

In the same time, Figure 13-indicate that average strain to failure increase significantly above temperatures between 800°C and 900°C for all compositions, showing slightly lower strains to failure above that temperatures in the samples containing larger amount of Si on A sub-lattice. For example, at 1000°C, Ti_3AlC_2 deformed up to 19% without failure, $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$ failed at 18% and Ti_3SiC_2 failed at 16% stain. In summary, results presented in Figure 13 suggest that around and above BPT, presence of Al in the A sub-lattice results in easier plastic deformation of individual grains (larger ductility), significant softening, and consequently more pounced decrease in compressive strength. The latter, also leads to the observed gradual weakening of the solid solution strengthening at and around BPT that was observed in $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$. Although the reason for observed effects of Al on the mechanical behavior of $\text{Ti}_3\text{Al}_{1-x}\text{Si}_x\text{C}_2$ phases is not completely clear at this point, it should be noted here that both mechanisms proposed to explain BPT in the MAX phases, namely grain boundary sliding and de-cohesion [2] and activation of secondary slip systems [56] would be most likely unaffected by substitution of Si by Al on the A sub-lattice. Therefore, it can be hypothesized that possible more pronounced softening of Ti-Al bonds in and higher mobility of Al promotes deformation by easier basal plane dislocation glide and formation of dislocation walls and low angle kink boundaries.

3.6 Oxidation of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ MAX phase solid solutions

To study the oxidation resistance of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions at elevated temperatures, Ti_3AlC_2 , $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$, and Ti_3SiC_2 are selected as candidates to oxidize at 1200°C for 1-100hrs. In this work, have measured the thickness of oxidation layer to evaluate oxidation resistance and kinetics [57]. Selected but typical FE-SEM images in Figure 14 a-c, together with EDSelemental line scans clearly demonstrate that the oxide layer formed on

Ti_3AlC_2 and $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ samples consist of almost pure alumina and have almost identical thickness, while on Ti_3SiC_2 , oxidizes forming very thick oxide layer at the same oxidation time that contains both TiO_2 and SiO_2 . A protective nature of alumina layer that forms during oxidation Ti_3AlC_2 and $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ can be even better illustrated in Figure 14 showing that the oxidation kinetics of $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ is almost identical to that of Ti_3AlC_2 , and significantly slower than that of Ti_3SiC_2 . Note here, that oxidation kinetic reported here are in good agreement with previously published results [57-60]. Results presented here further confirm that $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ would rather form pure alumina oxide layer than mixed TiO_2 , SiO_2 and Al_2O_3 oxide layers, thus providing an excellent oxidation resistance when compared with Ti_3SiC_2 as it was previously postulated elsewhere [23, 61].

4 Conclusion

A series of high-purity $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ MAX phase solid solutions with $x=0, 0.2, 0.4, 0.6, 0.8$, and 1 were reaction sintered from Ti, TiC, Al and Si powder mixtures using pulse electric current sintering (PECS) in the temperature range of $1500\text{-}1600^\circ\text{C}$. X-ray diffraction results revealed not only the high purity of all processed samples, but also that the c - lattice parameter decreases linearly with increasing amount of Si on the A sub-lattice while a -lattice parameter remains almost constant. The elastic moduli of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ were found to increase monotonically as x goes from 0 to 1 , while the specific heat capacity seems to be unaffected by the alloying on the A- site in this MAX phase solid solution system. However, coefficient of thermal expansion (CTE) of $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$ solid solution is lower than that of end members, due to stronger Si-Al interactions in A layer.

Regardless of the grain size, $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ shows ideal solid solution hardening behavior as compositions around $x=0.5$ have the highest Vickers hardness. Nevertheless, the

solid solution strengthening effect is a strong function of the grain size at room temperature, i.e. it is very mild in the fine grain structures with the maximum strength of solid solutions that is only up to 7- 8 % higher than that of end members. On the other hand, coarse grained solid solutions shows improved compressive strength for more than 30% relative to the end members. The effect of solid solutions strengthening diminish at around brittle-to-ductile transition temperatures, resulting in lower compressive strength of solid solutions when compared to Ti_3SiC_2 , but slightly higher to that of Ti_3AlC_2 . Finally, $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions possess excellent oxidation resistance as Ti_3AlC_2 due to the formation of continuous alumina layer on the surface. Results presented here suggest that alloying on the A sub-lattice can be used to strengthen $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ MAX phases with some limitations; i.e. it is most effective only below brittle-to-plastic transition temperature for the coarse grained microstructures. Although $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ forms protective alumina oxide scale above brittle-to-plastic transition temperature, solid solution strengthening effect above that temperature completely diminishes and their strength is significantly lower than that of the pure Ti_3SiC_2 .

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Table Captions

Table 1 The compositions and sintering conditions for $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ through Spark Plasma Sintering, where $x = 0-1$.

Table 2 Heat treatment condition for grain growth in ultra-purity argon flow.

Figure Captions

Figure 1 XRD patterns of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ after PECS, where $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 , respectively. Triangles and squares denote peak positions for Ti_3SiC_2 and Ti_3AlC_2 .

Figure 2 The c-lattice and a-lattice parameters as a function of Si content, which are obtained from XRD patterns in this study and first principle calculation in the previous work, respectively.

Figure 3 Typical SEM image under back scattered mode (a) of $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ and the elemental mapping results (b-d).

Figure 4 Average grain size (length and width) of (a) as-sintered samples; (b) after additional thermal treatment to promote grain growths. Error bars represent standard deviation. Inserts show typical SEM micrographs of etched surfaces that were used for grain size measurements.

Figure 5 The density and relative density of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ MAX phase solid solutions

Figure 6 The heat flow (a) and specific heat capacity (b) of as a function of temperature for selected $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ samples.

Figure 7 Displacement vs. temperature obtained using TMA in the temperature range of -25°C and 350°C and (b) is calculated as the coefficient of thermal expansion of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ and the end members as a function of temperature.

Figure 8 (a) The Young's modulus of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions as a function of Si content at room temperature, where calculated values are derived from DFT [30]; (b) The Young's modulus of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions as a function of temperature, where the dash line is the Young's modulus of two end members that are calculated from DFT[49].

Figure 9(a) Average Vickers hardness values for FG- and CG- $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ samples as a function of Si content. Error bars indicate standard deviation from 20 measurements. Calculated (theoretical) hardness is adopted from Son et al.[30]. (b) Selected but typical SEM image of the indent in $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$ after testing using 10N load.

Figure 10 Compressive strength of FG (grain length of 7 μm) and CG (grain length of 25 μm) $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions and the end members as a function of Si content. For comparison, compressive strengths of end members from literature are also plotted in this figure. Error bars denote standard deviation from 3-4 tests.

Figure 11 Photographs of the samples after testing in compression and SEM images on the fracture surfaces for (a) FG- Ti_3SiC_2 and (b) CG- $\text{Ti}_3\text{Al}_{0.6}\text{Al}_{0.4}\text{C}_2$ solid solution.

Figure 12 Typical stress-strain curves of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ solid solutions at high temperatures, where (a) is $x=0$; (b) is $x=0.4$ and (c) is $x=1$

Figure 13 (a) Compressive strength and (b) strain-to-failure of FG of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ samples with $x = 0, 0.4$ and 1 as a function of temperature. Error bars show standard deviations calculated from 3 tests. Vertical arrows in (b) denote maximum strains measured before the testes were stopped.

Figure 14 (a), (b) and (c) Backscattered electron FE-SEM images of oxide layers formed after oxidation of Ti_3AlC_2 , $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$, and Ti_3SiC_2 respectively, at 1200 °C for 10 hours. (d) Thickness of the oxide layer vs. oxidation time at 1200 °C. For comparisons, the dash line are previous experimental data for Ti_3AlC_2 from Zhou et al [58, 59] and Ti_3SiC_2 from Barsoum et al [60].

Figure 1 XRD patterns of $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ after PECS, where $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 , respectively. Triangles and squares denote peak positions for Ti_3SiC_2 and Ti_3AlC_2 .

Figure 2 The c-lattice and a-lattice parameters as a function of Si content, which are obtained from XRD patterns in this study and first principle calculation in the previous work, respectively.

Figure 3 Typical SEM image under back scattered mode (a) of $\text{Ti}_3(\text{Al}_{0.6}\text{Si}_{0.4})\text{C}_2$ and the elemental mapping results (b-d).

Figure 4 Average grain size (length and width) of (a) as-sintered samples; (b) after additional thermal treatment to promote grain grows. Error bars represent standard deviation. Inserts show typical SEM micrographs of etched surfaces that were used for grain size measurements.

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Figure 14 (a), (b) and (c) Back scattered electron FE-SEM images of oxide layers formed after oxidation of Ti_3AlC_2 , $Ti_3(Al_{0.6}Si_{0.4})C_2$, and Ti_3SiC_2 respectively, at 1200 °C for 10 hours. (d) Thickness of the oxide layer vs. oxidation time at 1200 °C. For comparisons, the dash line are previous experimental data for Ti_3AlC_2 from Zhou et al [58, 59] and Ti_3SiC_2 from Barsoum et al [60]

Table 1 The compositions and sintering conditions for $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ through Spark Plasma Sintering, where $x = 0-1$

x	Nominal composition of the powder mixture	Sintering conditions
0	Ti:Al:C=3:1.2:1.8	1510°C for 15min
0.2	Ti:Al:Si:C=3:0.96:0.24:1.8	1550°C for 15min
0.4	Ti:Al:Si:C=3:0.72:0.45:1.9	1560°C for 15min
0.6	Ti:Al:Si:C=3:0.45:0.73:1.9	1560°C for 15min
0.8	Ti:Al:Si:C=3:0.24:0.96:1.9	1580°C for 15min
1.0	Ti:Si:C=3: 1.2:1.85	1600°C for 15min

Table 2 Heat treatment condition for grain growth in ultra-purity argon flow.

Sample	Processing condition
x=0	1350°C for 24hr
x=0.4	1350°C for 24hr
x=0.6	1400°C for 28hr
x=1	1450°C for 24hr