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PII: S0925-8388(18)32139-X

DOI: [10.1016/j.jallcom.2018.06.027](https://doi.org/10.1016/j.jallcom.2018.06.027)

Reference: JALCOM 46363

To appear in: *Journal of Alloys and Compounds*

Received Date: 7 February 2018

Revised Date: 15 May 2018

Accepted Date: 3 June 2018

Please cite this article as: B. Velasco, E. Gordo, L. Hu, M. Radovic, S.A. Tsipas, Influence of porosity on elastic properties of  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  MAX phase foams, *Journal of Alloys and Compounds* (2018), doi: 10.1016/j.jallcom.2018.06.027.

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# Influence of porosity on elastic properties of $\text{Ti}_2\text{AlC}$ and $\text{Ti}_3\text{SiC}_2$ MAX phase foams

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## 1. Abstract

MAX phase foams could have various applications where tailored functional and mechanical properties are required. In this study,  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  MAX phase foams with controlled porosity and pore size were produced and characterized. The foams were produced from MAX phase powders by powder metallurgy method using crystalline carbohydrate as a space holder. Foams with overall porosity up to approximately 71 vol.% and pore size from 250  $\mu\text{m}$  to 1000  $\mu\text{m}$  were successfully produced; micro-porosity and macro-porosity was characterized. Poisson's ratio and elastic moduli of the foams were measured by resonant ultrasound spectroscopy (RUS) and analyzed as a function of porosity and pore size. Different models were used to fit the experimental data and interpret the effect of pore size and amount of porosity and on elastic properties. It was found that the amount and type of porosity has a larger influence on the elastic properties than the pore size.

## 2. Introduction

The MAX phases are ternary carbides or nitrides with general chemical formula  $\text{M}_{n+1}\text{AX}_n$  where M is an early transition metal, A is typically an A-group element, X is carbon or nitrogen and  $n=1, 2$  or  $3$ . [1, 2]. MAX phases are considered to be good candidate materials for numerous applications due to their unusual and sometimes unique set of properties [1,2]. As typical metals and alloys, the MAX phase show good damage tolerance and machinability, high thermal and electrical conductivity, and ability to plastically deform more than 25% at high temperatures, even in tension. However, like typical carbides, nitrides and most of other ceramics, they have excellent thermal stability, high stiffness, good corrosion and oxidation resistance, good high-temperature mechanical properties and creep resistance. In addition, they show hysteretic, non-linear elastic stress-strain behavior and can dissipate significant portion of strain energy during cyclic loading even at room temperatures [3–5]. The origin of these unusual properties lies in the nature of their atomic bonds and nano-layered atomic structure [1,2,6].

Over the last two decades, most of the studies have reported on processing, structure and properties of fully dense MAX phases and only a limited number of studies investigated porous ones. Pressureless sintering has been used to produce  $\text{Ti}_2\text{AlC}$  with porosities as low as 10 vol%. [7]. Porous  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{AlC}_2$  with up to 80 vol.% porosity, have been also processed using the replication method [8, 9]. Most recently, porous  $\text{Ti}_2\text{AlC}$  with porosity up to 93 vol.% has been produced by gel casting technique using agarose as a gelling agent to consolidate the foam structure [10]. Reactive sintering of elemental powders in a vacuum furnace has been used to process porous  $\text{Ti}_3\text{SiC}_2$  with porosity ranging from 28 vol.% to 42 vol.% [11,12]. This processing method has also been employed to produce porous MAX phase composites of  $\text{Ti}_3\text{SiC}_2/\text{TiC}$ ,  $\text{Ti}_3\text{AlC}_2/\text{TiC}$ , and  $\text{T}_4\text{AlN}_3/\text{TiN}$  from various powder mixtures

with porosities ranging from 5 vol.% to 35 vol.% [13]; in another study the same group produced porous 70%Ti<sub>3</sub>SiC<sub>2</sub>/30%TiC composite by reactive sintering, and demonstrated that porous materials exhibit higher specific strength than fully dense Ti<sub>3</sub>SiC<sub>2</sub> [14]. In recent years, the space holder method, adding NaCl particles [15,16] or sugar crystal particles [17,18] has been employed to produce Ti<sub>2</sub>AlC [15,17,18] and Ti<sub>3</sub>SiC<sub>2</sub> [16] foams, because this method allows not only easy processing of materials with different overall porosity, but at the same time good control of pore sizes.

There is an increasing interest in porous MAX phases with an emphasis on tuning porosity to tailor mechanical properties [7,11,15,20] or using them as preforms for composite materials [20–23]. It has been demonstrated that the thermal and mechanical properties of Ti<sub>2</sub>AlC and Ti<sub>3</sub>SiC<sub>2</sub> decrease with increasing porosity [7,11,15,20]. Previous studies showed that increasing porosity decreases the threshold stresses needed for the formation of kinking bands and subsequently decreases the strength and stiffness of the material [15]. For Ti<sub>3</sub>SiC<sub>2</sub> the variation of porosity from 0 vol.% up to 55 vol.% leads to the decrease of the ultimate compressive strength from 1300 MPa up to 60 MPa respectively [20]; similar tendency is reported for Young's modulus which decreases from 325 GPa to 26 GPa for samples with porosity ranging from 0 vol.% up to 55 vol.% [20].

In foams, control of pore size and distribution from the processing stage is of outermost importance in order to tailor their final properties. Overall density is the most important parameter affecting elastic properties of the foam [24,25], although Young's moduli of cellular structures are also known to be strongly linked to the architecture of the cellular material [25]. However, there are only few reports on the effects of porosity on the elastic properties of MAX phases, despite the importance it has for structural applications. Young's moduli of porous Ti<sub>2</sub>AlC and Ti<sub>3</sub>SiC<sub>2</sub> have been reported for porosity up to 40.5 vol.% for Ti<sub>2</sub>AlC [15] and 55 vol.% for Ti<sub>3</sub>SiC<sub>2</sub> [20].

This work reports on the effect of porosity on elastic properties of MAX phase foams, namely Ti<sub>2</sub>AlC and Ti<sub>3</sub>SiC<sub>2</sub>. Elastic properties were evaluated not only as a function of porosity but also as a function of pore size distribution. The experimental data were fitted with different existing models over the whole range of porosity. Most existing models used for the prediction of elastic properties only take into consideration limited porosity ranges and do not account for pore size. In this work, experimental elastic properties were fitted over a very wide range of porosity and fitting parameters are related to the microstructure of the porous MAX phases. The technique used in this study to process the foams from the starting MAX phase powders was the space holder technique employing a crystalline carbohydrate as space holder. Different ratios of space holder-powders were selected in order to study the effect of porosity on the properties. Also, different space holder size distributions were introduced in order to study the effect of the pore size on the elastic properties. Characterization of the materials processed with and without space holder included: the phase stability, microstructure and porosity measurements by Archimedes method and image analysis. Elastic properties, namely Young's modulus, bulk modulus and Poisson's ratio, were studied using Resonant Ultrasound Spectroscopy (RUS) and related to the porosity.

### 3. Materials and Methods

In this study two commercial powders were used, namely Ti<sub>2</sub>AlC and Ti<sub>3</sub>SiC<sub>2</sub> (Kanthal, a Sandvik brand, Sweden) to prepare the MAX phase foams. The particle size distribution of the starting powders was determined to be in: D<sub>50</sub>=9.801 μm for Ti<sub>2</sub>AlC and D<sub>50</sub>=5.582 μm for Ti<sub>3</sub>SiC<sub>2</sub> using a Mastersizer 2000 (Malvern Instruments, UK) particle size analyzer.

The powders were mixed with a 2% solution of Acrawax C:  $C_{38}H_{76}N_2O_2$  binder (Lonza, Switzerland) to facilitate their compaction. The white sugar powder (Azucarera of AB Sugar, United Kingdom) was used as a space holder. It was first sieved to yield powders with three particle size distributions: 250-400  $\mu\text{m}$ , 400-800  $\mu\text{m}$  and 800-1000  $\mu\text{m}$ . White sugar powders with different size distributions were then mixed with MAX phase powders in three different volume ratios: 0.2, 0.4 and 0.6. This resulted in nine different mixtures of both  $Ti_2AlC$  and  $Ti_3SiC_2$  powders using three different volume fractions of white sugar powders, each with three different particle size distributions. The mixtures were then poured inside a silicone mold, sealed and then submerged in the hydraulic oil of a cold isostatic presses (CIP, EPSI, Belgium) and pressed at 400 MPa for 10 minutes. The green bodies were weighted by a balance with resolution of  $\pm 0.0001$  g (Mettler Toledo, Spain) to record their mass including the sugar space holder. The green bodies, prior to sintering, were soaked in distilled water at 70 °C for 48 hours to remove the space holder. Subsequently, they were dried at 30 °C for 24 hours. After the removal of the space holder, the mass of the samples was measured again in order to confirm the completion of the space holder dissolution process. The samples were then sintered in vacuum ( $10^{-5}$  mbar) at 1400 °C for  $Ti_2AlC$  and 1350 °C for  $Ti_3SiC_2$ , for 4 hours in a tube furnace (Carbolite, Germany). During heating, all samples were held at 400 °C for 30 minutes to burn out any space holder residue in the samples. The samples were machined into a cylindrical shape with a lathe to obtain a uniform geometry: a constant diameter along the long direction and parallel bases. Porosity was calculated on machined samples by both Archimedes' principle and measuring the dimensions and mass. The Archimedes' principle was used following the ASTM C20-00 standard and using ethanol to infiltrate the samples and as immersion medium, using procedure described in more detail elsewhere [13,17,18] and using the following equations:

$$\rho = \frac{\text{dry mass} \cdot \rho_{\text{ethanol}}}{\text{wet mass} - \text{suspended mass}} \quad (1)$$

$$\text{Porosity}_{\text{overall}}(\%) = \left(1 - \frac{\rho}{\rho_{\text{teoretical}}}\right) \cdot 100 \quad (2)$$

$$\text{Porosity}_{\text{open}}(\%) = \left(\frac{\text{wet mass} - \text{dry mass}}{\text{wet mass} - \text{suspended mass}}\right) \cdot 100 \quad (3)$$

$$\text{Porosity}_{\text{closed}}(\%) = \text{Porosity}_{\text{overall}}(\%) - \text{Porosity}_{\text{open}}(\%) \quad (4)$$

where “dry mass” is the mass (in g) of the dry sample, “wet mass” is the mass of the sample after soaking in ethanol during 2 hours, “suspended mass” is the mass of the sample suspended in ethanol using a suspending system,  $\rho_{\text{ethanol}}$  is the density ( $\text{g}/\text{cm}^3$ ) of ethanol,  $\text{Porosity}_{\text{overall}}$  is the volume fraction of the overall porosity (vol.%) of the sample,  $\text{Porosity}_{\text{closed}}$  is the volume fraction (vol. %) of the closed porosity if the sample and  $\text{Porosity}_{\text{open}}$  is volume fraction of the open porosity of the sample. The density of the starting powder ( $\rho_{\text{teoretical}}$ ) was determined by helium pycnometer (Accupyc 1330, Micromeritics, USA).

The phase composition of sintered samples was studied by X-Ray Diffraction (XRD) using X'Pert Diffractometer (Phillips, Holland) with  $\text{Cu } K_{\alpha}$  radiation (wavelength = 1.542 Å) at 40 kV and 30 mA in the  $2\theta$  range from  $8^{\circ}$  to  $80^{\circ}$  with a step size of  $0.04^{\circ}$  and a step time of 1.5 s. The data was analyzed using Inorganic Crystal Structure Database (ICSD) and Powder Diffraction File (PDF-2) database. The phase stability was studied by doing XRD analysis in three conditions of the material: raw powder, sintered with, and without space holder. The molar fraction of the phases was calculated by the relationship of  $I_x/I_t$  where  $I_x$  is the integrated intensity of highest representative peak of each phase and  $I_t$  is sum of the integrated intensities for the highest representative peaks of all the constituent phases of

the material. The mass loss after sintering expresses the mass variation of the green body compared to that in the sintered state.

The samples were cut, mounted in resin, and then ground and polished with 1  $\mu\text{m}$  diamond abrasive for metallographic observation. The microstructural images were obtained by a scanning electron microscope (SEM; Philips XL-30, with filament of W) using the accelerating voltage and emission current of 15 kV and 20 mA, respectively.

Image analysis was performed on SEM images using image-j software. For each foam, the image analysis was performed following the ASTM E112-12 standard on at least 3 images from three different areas. For samples with bigger space holder size range (800-1000  $\mu\text{m}$ ) the entire cross section was analyzed due to the limited number of pores in each image. Magnification of 2500x was used to study the porosity within the struts in the foam and magnification of 65x to study the porosity introduced by the space holder. The equivalent circular diameter (ECD) as the diameter of an equivalent circle with the same area as the pore cross-section area was calculated using the following equation [26]:

$$ECD = \sqrt{\frac{4A}{\pi}} \quad (5)$$

where A is the pore area. The ECD was determined for each pore in different foams. The median value of the ECD, for each sample was determined as the value at the cumulative frequency of 50%.

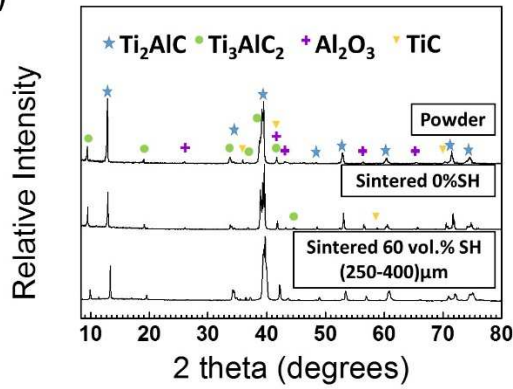
The elastic properties and Poisson' ratio were determined by resonant ultrasound spectroscopy (RUS; Magnaflux Quasar Systems, NM) using procedure described in more detail elsewhere [15,27,28]. The collected resonant spectra were analyzed using Quasar RuSpec software (Magnaflux Quasar Systems, NM) that iteratively calculates resonant peaks of the isotropic sample assuming different values of elastic constants (C11 and C44), until they converge closely the measured resonant frequencies of the sample with known geometry and mass. The criterion for accepting the determined elastic constants through described iterative process was a root-mean-square error (RMSE) between calculated and measured positions of resonant peaks below 0.50%.

## 4. Results

### 4.1 Microstructural Characterization and Porosity Measurements

The phase composition of the starting material and the processed foams was investigated by XRD. XRD results in Figure 1a show that the starting  $\text{Ti}_2\text{AlC}$  powder contains two major phases ( $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{AlC}_2$ ) and two minor phases ( $\text{TiC}$  and  $\text{Al}_2\text{O}_3$ ). The same phases were identified in the sintered samples with and without space holder and agree with the phases commonly observed in this material. The molar fractions of identified phases determined from XRD results are shown in Table 1. There is a slight decrease of the amount of  $\text{Ti}_2\text{AlC}$  after sintering in both cases, with and without space holder.

a)



b) USCRIP

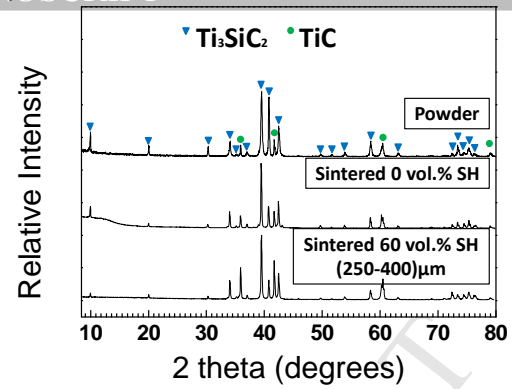


Figure 1. XRD results of the raw powder, sintered material without space holder and with 60 vol.% space holder for a)  $\text{Ti}_2\text{AlC}$  and b)  $\text{Ti}_3\text{SiC}_2$ . The identification is performed using Inorganic Crystal Structure Database (ICSD: 165460 for  $\text{Ti}_2\text{AlC}$ , 153266 for  $\text{Ti}_3\text{AlC}_2$ , 10425 for  $\text{Al}_2\text{O}_3$ , and 44495 for  $\text{TiC}$ ) and to the Powder Diffraction File (PDF-2: 01-074-0310 for  $\text{Ti}_3\text{SiC}_2$  and 03-065-0242 for  $\text{TiC}$ ).

Table 1. Comparison of the molar fractions of the four phases for the  $\text{Ti}_2\text{AlC}$  material in three different conditions: raw powder, sintered with 0 vol.% and with 60 vol.% space holder.

Phase	Molar fraction (%)		
	Raw	Sintered	Sintered
	Powder	0 vol.% space holder	60 vol.% space holder
$\text{Ti}_2\text{AlC}$	63	59	54
$\text{Ti}_3\text{AlC}_2$	25	31	29
$\text{TiC}$	6	5	9
$\text{Al}_2\text{O}_3$	6	5	8

Figure 1b shows the XRD results for the  $\text{Ti}_3\text{SiC}_2$ . The initial powder contains  $\text{Ti}_3\text{SiC}_2$  as the major phase and  $\text{TiC}$  as the minor phase. No other phases were identified by the XRD neither in the material sintered using space holder nor in the material sintered without using space holder. Table 2 shows the molar fractions of the phases identified in the  $\text{Ti}_3\text{SiC}_2$  samples. After sintering, no difference in the molar fractions of the phases can be observed for the sample without space holder. For the sample sintered using 60 vol.% space holder, the amount of  $\text{TiC}$  phase increases 16% after sintering. In order to investigate the origin of observed phase changes in those samples, the mass loss during sintering of the  $\text{Ti}_3\text{SiC}_2$  foam was monitored and results are summarized in Figure 2. It is clear from Figure 2 that mass loss increases from 3.69 % to 6.84 % as the volume of space holder increases from 0 vol.% to 60 vol.%.



Table 2. Comparison of the molar percentages (%) of the phases for the  $Ti_3SiC_2$  material in three different conditions: raw powder, sintered with 0% space holder and with 60% space holder.

Phase	Molar fraction (%)		
	Raw Powder	Sintered 0% SH	Sintered 60% SH
$Ti_3SiC_2$	79	79	63
TiC	21	21	37

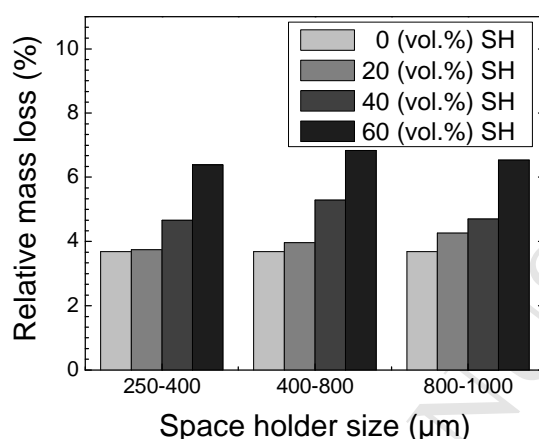
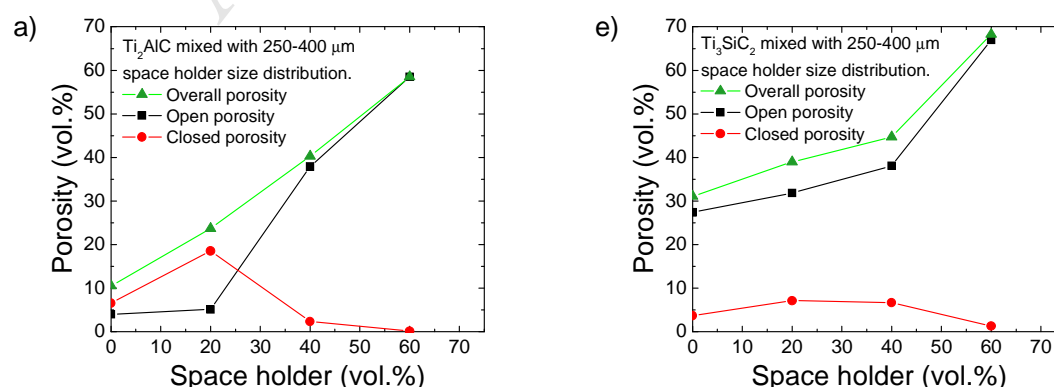
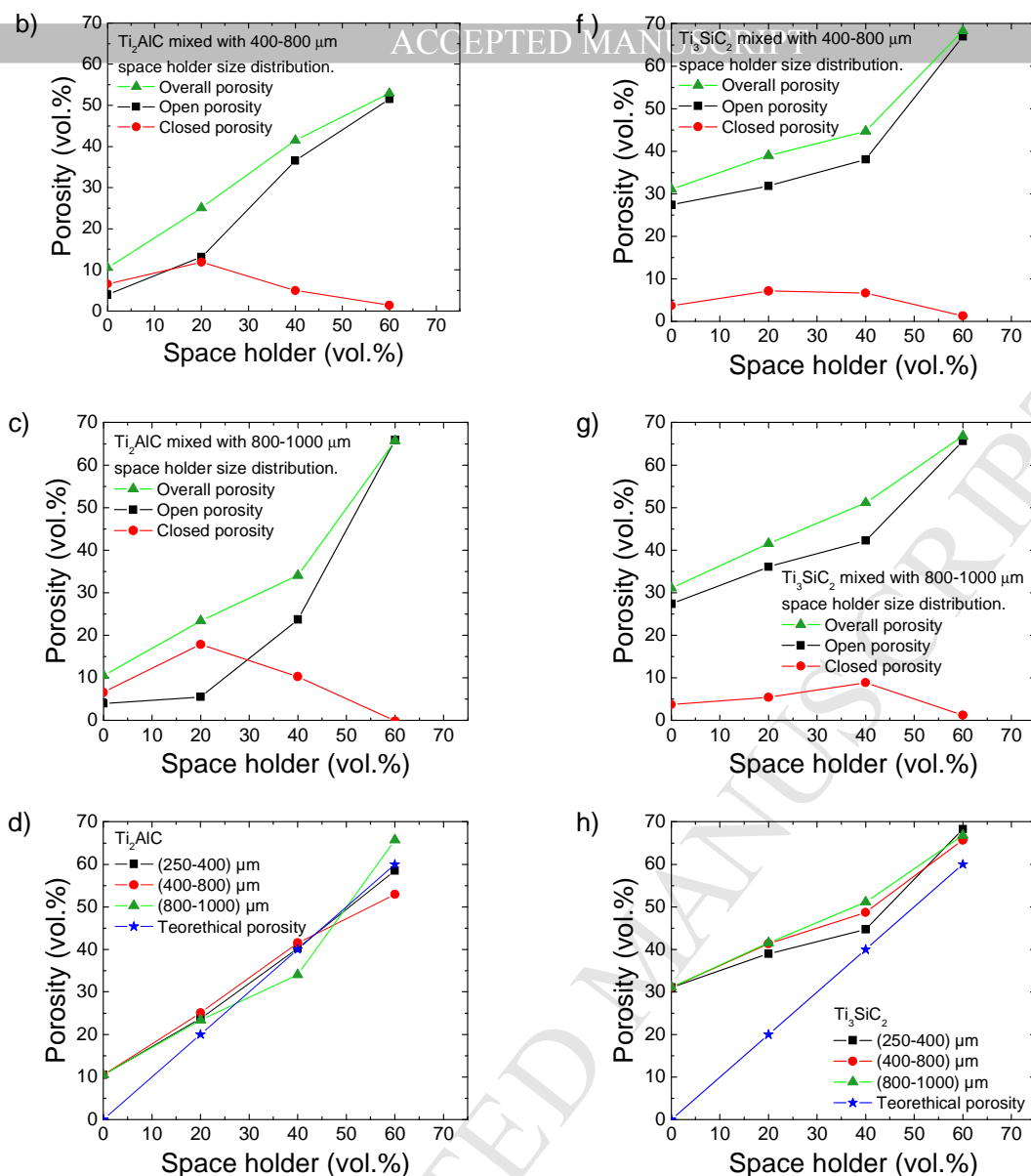


Figure 2. The mass loss (%) during the sintering of the  $Ti_3SiC_2$  material with three volume ratios of space holder (20 vol.%, 40 vol.% and 60 vol.%) and three space holder size ranges (250-400  $\mu m$ , 400-800  $\mu m$  and 800-1000  $\mu m$ ) in comparison with the material without space holder.

Overall, open, and closed porosities in all processed foams were determined using Archimedes' method and results are summarized in Figure 3 for both  $Ti_2AlC$  (Figures 3a-d) and  $Ti_3SiC_2$  (Figures 3e-h) foams with different volume fractions of the space holder. Note that results in Figure 3 also show overall, open and closed porosities in samples sintered without using any space holder at the same sintering conditions. In addition, the overall nominal porosity is compared to the experimental one for the three space holder with different particle size ranges in Figures 3d and 3h for both  $Ti_2AlC$  and  $Ti_3SiC_2$  foams, respectively. The nominal porosity was calculated assuming that the overall porosity is equal to volume fraction of the space holder used during processing.





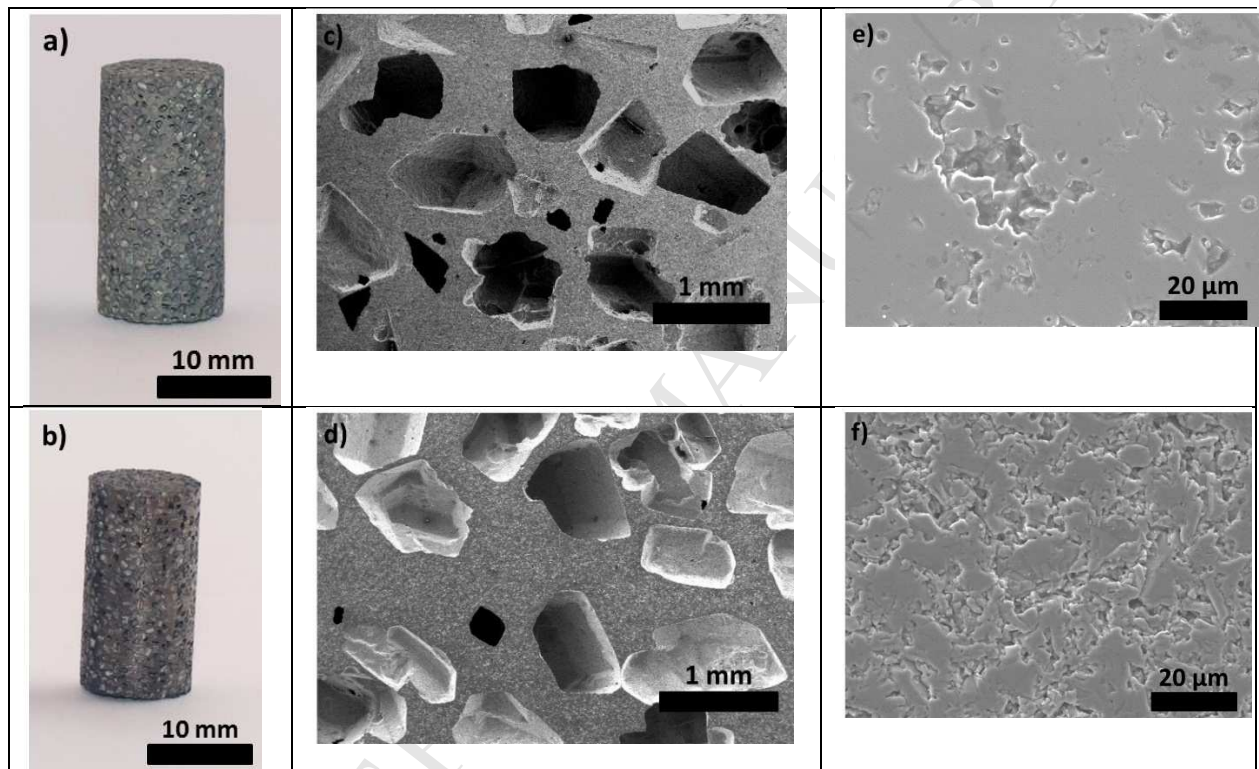
Figures 3. Overall, open and closed porosity measured by Archimedes' method for different space holder size ranges.; a)  $Ti_2AlC$  foams with 250-400  $\mu m$ , b)  $Ti_2AlC$  400-800  $\mu m$ , c)  $Ti_2AlC$  800-1000  $\mu m$ , e)  $Ti_3SiC_2$  250-400  $\mu m$ , f)  $Ti_3SiC_2$  400-800  $\mu m$ , g)  $Ti_3SiC_2$  800-1000  $\mu m$ . Comparison between theoretical and experimental porosity for: d)  $Ti_2AlC$  and h)  $Ti_3SiC_2$  with three space holder size ranges.

Figures 3a-3d show that  $Ti_2AlC$  samples sintered without space holder have 10% of mostly closed porosity. Those pores are around a micron-size (Figures 4e and 4f) and appear not only in the samples sintered without using space holder, but also in the struts of all foams processed using different volume fractions of space holder. For samples processed using 20 vol.% or more of space holder, overall porosity ( $P$ ) is always larger than open porosity ( $P_{open}$ ), which is, in turn, always larger than closed porosity ( $P_{closed}$ ), i.e.  $P > P_{open} > P_{closed}$ . While closed porosity remains always below ~20 vol.% and decreases with amount of space holder, open porosity increases with amount of space holder, regardless of space holder size range.  $Ti_3SiC_2$  samples without space holder show around 31% porosity, Figures 3e-3h. The porosity is mainly open and  $P > P_{open} > P_{closed}$ . The open porosity increases with increasing amount of space holder regardless of the space holder particle size range.



Figure 3d and 3h show the differences between experimental and theoretical porosities. For samples with 0 vol.% of space holder, the difference between measured and theoretical porosity is higher for  $\text{Ti}_3\text{SiC}_2$  than for  $\text{Ti}_2\text{AlC}$ , because of higher incomplete densification of the samples during pressureless sintering. For samples processed with 40 vol.% of space holder or more, the measured porosity is close to the theoretical one.

For  $\text{Ti}_2\text{AlC}$ , experimental and theoretical porosities are very close to each other, suggesting that most of the porosity is generated by space holder.  $\text{Ti}_3\text{SiC}_2$  samples show a larger difference between experimental and theoretical porosity due to the fact that the foam cell walls (or struts) in  $\text{Ti}_3\text{SiC}_2$  contain more micron-sized pores than in  $\text{Ti}_2\text{AlC}$  foams. For both materials, experimental porosity tends to be closer to the calculated one as the amount of space holder increases. This occurs because relative contribution of porosity from cell walls (micrometer-sized pores) decreases with increasing macro porosity introduced by space holder.



*Figure 4. Representative images of foams of both materials containing 60 vol.% space holder and with 800-1000  $\mu\text{m}$  space holder size distribution in three different magnifications: a) macrophotograph of  $\text{Ti}_2\text{AlC}$  foam, b) macrophotograph of  $\text{Ti}_3\text{SiC}_2$  foam; c) characteristic SEM image of the microstructure of  $\text{Ti}_2\text{AlC}$  foam d) characteristic SEM image of the microstructure of  $\text{Ti}_3\text{SiC}_2$  foam; e) cell-wall of  $\text{Ti}_2\text{AlC}$  foam and f) cell-wall of  $\text{Ti}_3\text{SiC}_2$  foam;*

Figures 4e and 4f show selected but typical images of the microstructure of the cell walls (or struts) in  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  foams. Both materials have micron-sized pores that are homogeneously distributed in the cell walls, but  $\text{Ti}_3\text{SiC}_2$  foams contains a larger amount of those pores (Figures 4e and 4f) than  $\text{Ti}_2\text{AlC}$  foams.

The millimeter-sized pores (macro pores) introduced by the space holder (Figures 4c and 4d) replicates the space holder's shape. The porosity is randomly and homogeneously distributed. Similar size and amount of porosity is achieved in both materials with the same volume percent and particle size range of space holder. Photographs of the foams are also shown in Figures 4a and 4b, for  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  foams, respectively. The foams have been

machined to a cylindrical shape in order to perform RUS measurements. The homogeneity and integrity of all foams is evident, including the foams with the highest amount of space holder.

The Equivalent Circular Diameter (ECD) of micron-sized pores in the cell walls was determined to better understand the influence of the space holder on their size (Figure 5). The ECD of micron-sized pores was found to be in  $\sim 1.5 \mu\text{m}$  in both  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  samples. Results in Figure 5 indicate that addition of space holder does not affect the size of micron-sized pores, i.e. it barely changes with increasing both volume fraction and particle size of space holder. These results show that the micron-sized pore size is insensitive to the size and amount of space holder, and confirm that they are formed as a result of incomplete deification during pressureless sintering.

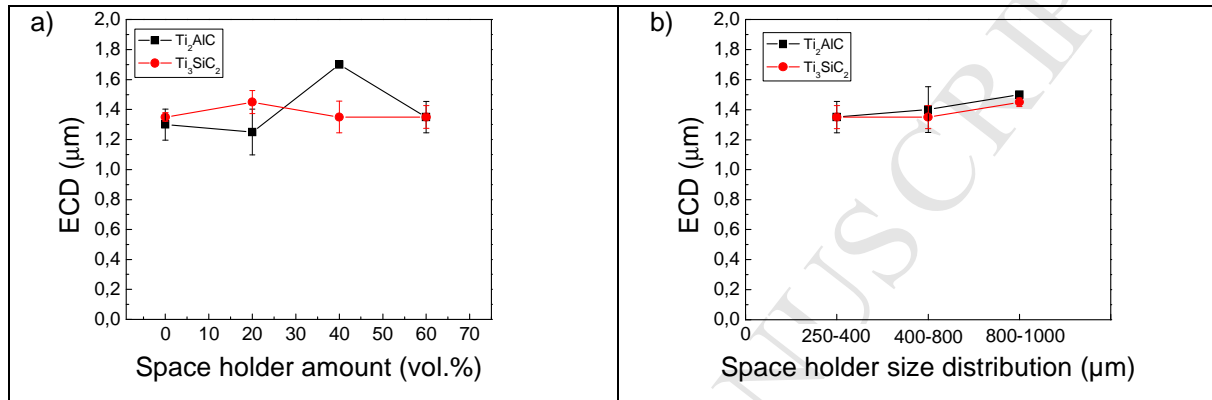


Figure 5. Median value ECD ( $\mu\text{m}$ ) of the micrometer-size pores for the materials  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  with respect to a) space holder volume fraction (for space holder size 250-400  $\mu\text{m}$ ) and b) size ranges (for 60 vol% space holder).

Figure 6 shows the porosity determined by analysis of SEM images of  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  foams processed using space holder with 250-400  $\mu\text{m}$  particle sizes. Note that results in Figure 6 are provided for micron-sized pores in the cell wall and for macro pores introduced by the space holder. Results in Figure 6 agree in general with the trends observed from measurements using Archimedes' method (Figure 3), with a difference in porosity between two different measurement methods of 0.4 %-7% for  $\text{Ti}_2\text{AlC}$  and 1%- 11% for  $\text{Ti}_3\text{SiC}_2$ . For both  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$ , results in Figure 6 once again confirm that the amount of macro pores increases almost linearly as the amount of space holder increases, although it is always slightly lower than the volume fraction of the space holder used in foam processing. The amount of micro-sized pores decreases as the amount of space holder increases (Figure 6), which is also consistent with previous results in Figure 3.

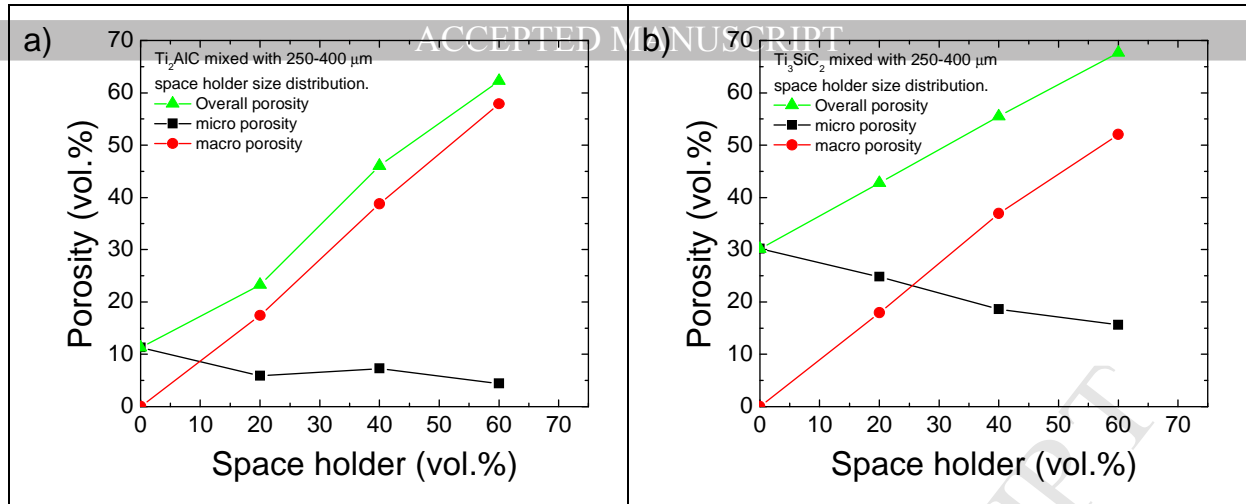


Figure 6. Porosity measured by image analysis for micron-size and macro pores in a)  $\text{Ti}_2\text{AlC}$  and b)  $\text{Ti}_3\text{SiC}_2$  foams, both processed using space holder with 250-400  $\mu\text{m}$  particle size.

#### 4.2 Elastic properties

The elastic properties were measured for all samples, including foams with porosity as high as 71 vol.%. Note here that all processed foams were strong enough to be handled and machined successfully in cylindrical samples with high dimensional precision that is needed to perform reliable RUS testing. Figure 7 and 8 show Young's (E) and shear (G) moduli of  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  foams, respectively, determined by RUS as a function of porosity. For comparison, Figures 7 and 8 also show elastic moduli of fully dense  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  previously published in literature [7,29], as well as those previously reported for porous samples manufactured by SPS [15,29], HIP [20] and space holder method with NaCl [15].

The experimental data obtained in this study (Figures 7 and 8) have been fitted using four different models, namely exponential model [30,31], Hasselman model [32], composite sphere model (CSM) [33–35] and the percolation model [36–38]. Note that for performing the fitting, the values for the fully dense materials were taken from previously published results [7,29]. The expressions used in each case are given below:

Exponential model [30,31]:

$$\frac{E}{E_0} = \frac{G}{G_0} = e^{-a \cdot P} \quad (6)$$

Hasselman model [32]:

$$\frac{E}{E_0} = \frac{G}{G_0} = 1 - \frac{aP}{1+(a-1)P} \quad (7)$$

Composite Sphere model (CSM) [33–35]:

$$\frac{E}{E_0} = \frac{G}{G_0} = \frac{(1-P)^2}{1-aP} \quad (8)$$

Percolation model [36–38]:

$$\frac{E}{E_0} = \frac{G}{G_0} = (1 - aP)^n \quad (9)$$

where  $E_0$  and  $G_0$  are the Young's and the shear moduli of fully dense material, respectively,  $P$  is overall porosity, and  $a$  and  $n$  are constants. In the CSM model, the constant  $a$  depends on the modulus and is a function of Poisson's ratio of the corresponding dense solid[34]. For the percolation model,  $a$  can be defined as  $a = 1/P_c$ , where  $P_c$  is the porosity at which the effective modulus becomes equal to zero. The constant  $n$  depends on the materials

properties and porous microstructure. The minimum value of  $a$  for the percolation model is 1 corresponding to a  $P_c=1$ .

The results of the fitting using all four models (Equations 6-9) are summarized in Tables 3 and 4, together with the coefficient of regression  $R^2$ . The experimental data of this study were compared to those found in literature for  $Ti_2AlC$  and  $Ti_3SiC_2$  foams. The data of elastic properties of foams from literature plotted in figures 8 and 9 for comparative purpose corresponds to foams that were manufactured in different ways including SPS [15,29], HIP [20] and space holder method with NaCl [15] and hence resulted in foams with different pore morphology and pore size. The data for fully dense materials from the literature are as following: Young's moduli of 277.6 GPa [7] and 343 GPa [29] for  $Ti_2AlC$  and  $Ti_3SiC_2$  respectively and the shear moduli of 118.8 GPa [29] and 143.8 GPa [29] for  $Ti_2AlC$  and  $Ti_3SiC_2$  respectively.

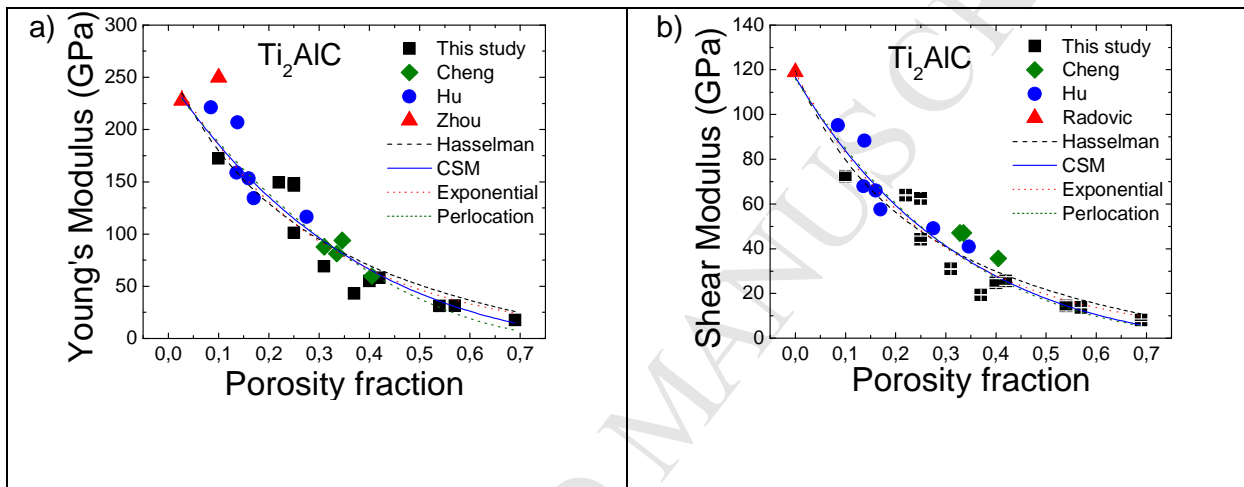


Figure 7. Variation of a) young's modulus and b) shear modulus elastic properties of  $Ti_2AlC$  with porosity in comparison to data previously published by Cheng [39], Hu [15] Zhou [7] and Radovic [29]. Solid, dotted and dashed lines are results of fitting using exponential [30,31], Hasselman [32], CSM [33–35] and the percolation [36–38].

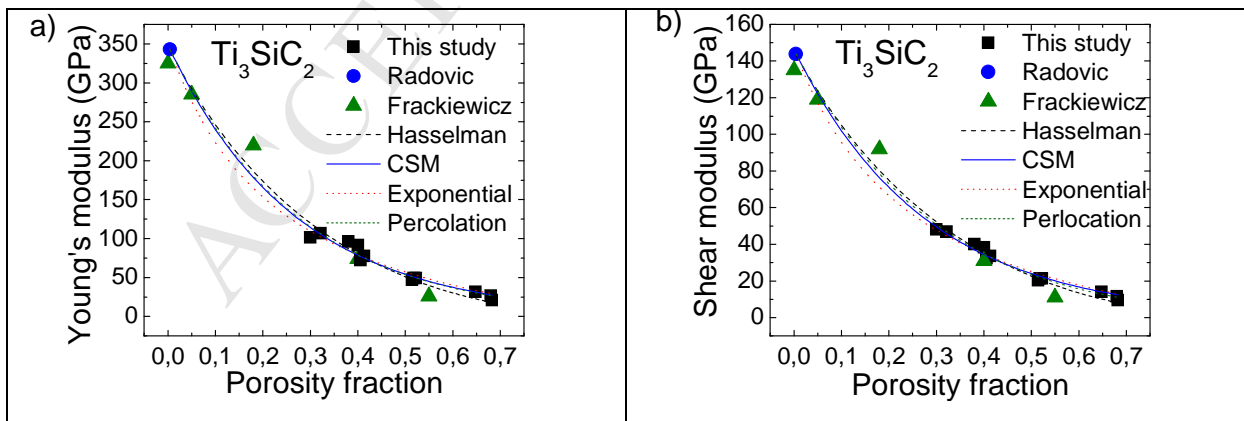


Figure 8. Variation of a) young's modulus and b) shear modulus elastic properties of  $Ti_3SiC_2$  with porosity in comparison to data previously published by Frackiewicz [20] and Radovic [29]. Solid, dotted and dashed lines are results of fitting using exponential [30,31], Hasselman [32], CSM [33–35] and the percolation [36–38] models.

Table 3. Result of fitting data in Figure 7 for  $Ti_2AlC$ , using exponential [30,31], Hasselman [32], CSMS [33–35] and percolation [36–38] models.

Model	E				G			
	a	$E_0$	n	$R^2$	a	$G_0$	n	$R^2$
Exponential	$3.4 \pm 0.4$	$260 \pm 22$	-	0.89	$3.6 \pm 0.3$	$119 \pm 8$	-	0.92
CSM	$0.9 \pm 0.5$	$249 \pm 22$	-	0.90	$1.3 \pm 0.5$	$117 \pm 8$	-	0.93
Hasselman	$4.1 \pm 1.0$	$262 \pm 29$	-	0.88	$4.5 \pm 0.8$	$119 \pm 9$	-	0.91
Percolation	$1.1 \pm 0.5$	$245 \pm 22$	$2.2 \pm 1.4$	0.90	$1 \pm 0.7$	$116 \pm 8$	$3.2 \pm 2.9$	0.92

Table 4. Result of fitting data in Figure 8 for  $Ti_3SiC_2$ , using exponential [30,31], Hasselman [32], CSMS [33–35] and percolation [36–38] models.

Model	E				G			
	a	$E_0$	n	$R^2$	a	$G_0$	n	$R^2$
Exponential	$3.7 \pm 0.1$	$348 \pm 7$	-	0.99	$3.6 \pm 0.1$	$147 \pm 2$	-	0.99
CSM	$1.4 \pm 0.2$	$346 \pm 9$	-	0.99	$1.2 \pm 0.1$	$145 \pm 3$	-	0.99
Hasselman	$5.1 \pm 0.3$	$351 \pm 8$	-	0.99	$4.9 \pm 0.2$	$147 \pm 3$	-	0.99
Percolation	$1.0 \pm 0.3$	$342 \pm 15$	$3.1 \pm 1.4$	0.97	$1.0 \pm 0.3$	$144 \pm 5$	$3 \pm 1$	0.98

Figures 9 and 10 show variations of E and G with porosity, for  $Ti_2AlC$  and  $Ti_3SiC_2$  foams, respectively, processed using space holder with different particle size ranges, together with results of fitting using CSM model.

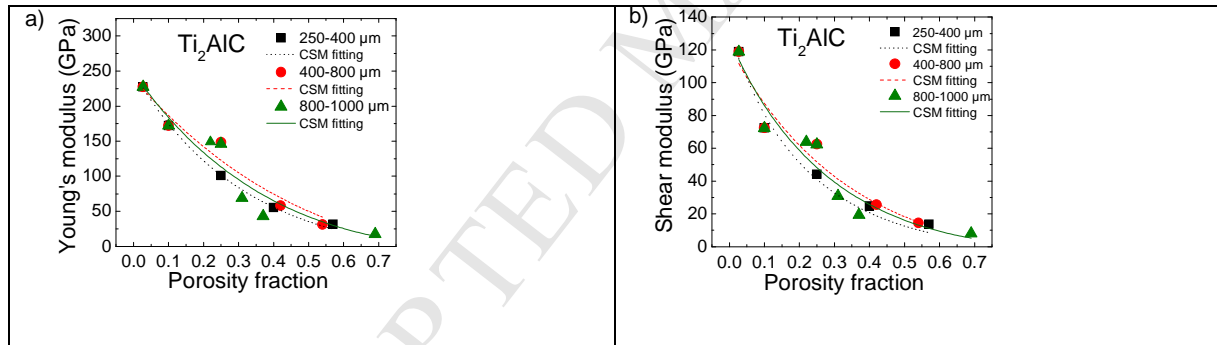


Figure 9. Variation of a) E and b) G with porosity for  $Ti_2AlC$  using three space holder size ranges: 250-400  $\mu m$ , 400-800  $\mu m$  and 800-1000  $\mu m$  and fitting for the composite sphere model [33–35]. For fully dense materials the data has taken from the literature: Young's modulus 277.6 GPa [7] and shear modulus: 118.8 GPa [29]

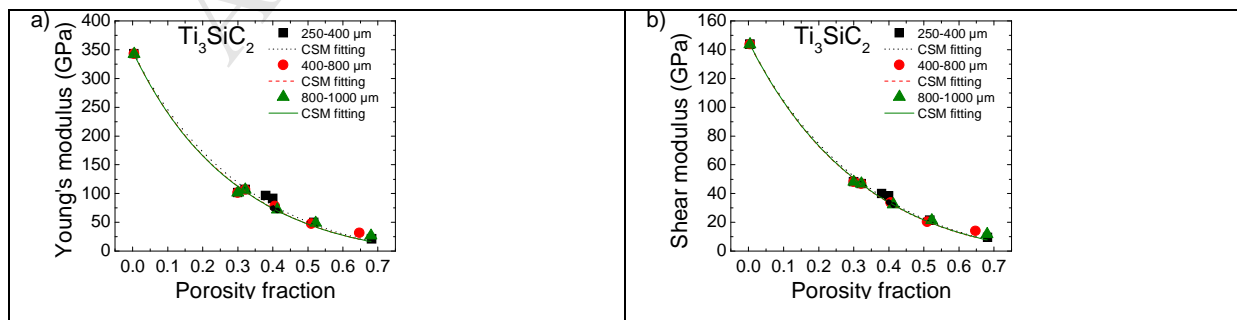


Figure 10. Variation of a) E and b) G with porosity for  $Ti_3SiC_2$  employing three space holder size ranges: 250-400  $\mu m$ , 400-800  $\mu m$  and 800-1000  $\mu m$  and fitting for the composite sphere model [33–35]. Young's modulus: 277.6 GPa [7] and the shear modulus: 118.8 GPa [29]. For



Figure 11a shows the Poisson's ratio determined for porous  $\text{Ti}_2\text{AlC}$  together with the values found in literature for samples produced using with different techniques [6,15,29,40]. The different pore sizes don't show a clear tendency in the behavior. Figures 11b shows the variation of Poisson's ratio with porosity for  $\text{Ti}_3\text{SiC}_2$ . Both materials show that Poisson's ratio decreases slightly with porosity.

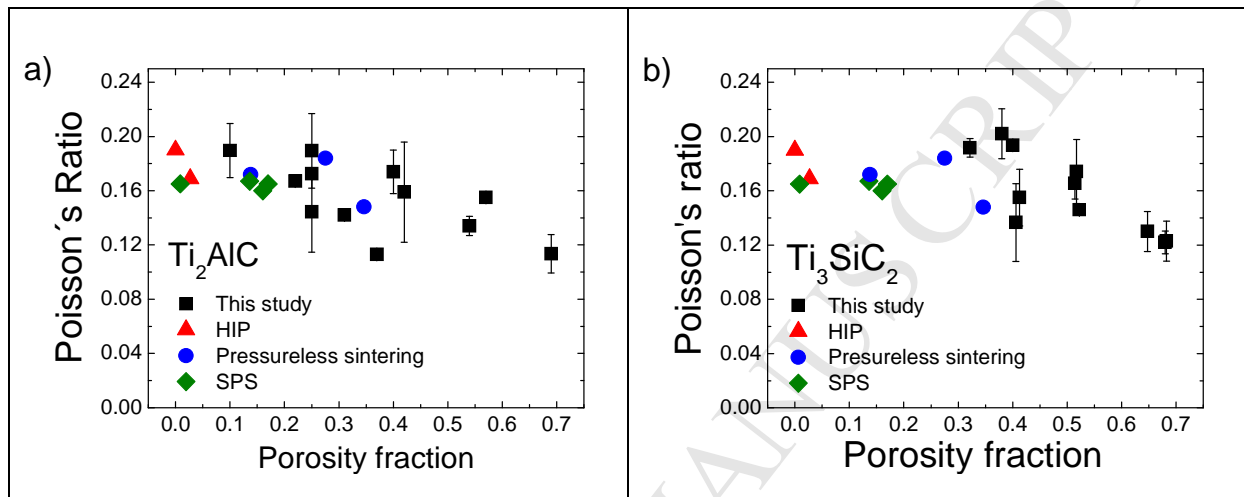


Figure 11. Experimental results of Poisson's ratio versus porosity for: a)  $\text{Ti}_2\text{AlC}$  and b)  $\text{Ti}_3\text{SiC}_2$  and comparison with the published by HIP [6,40], Pressureless sintering [15] and SPS [29].

## 5. Discussion

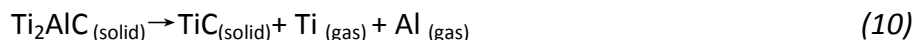
### 5.1 Phase stability

The results presented in this paper shows clearly that soluble crystalline carbohydrate can be used for easy processing of  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  foams with up to 60% porosity and tailoring pore sizes and thus elastic properties of MAX phase foams. For both  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  foams slight compositional differences can be observed between the as-received powders, the sintered powders without space holder and the foam materials, as it is shown in Figure 1 and Table 1. These compositional differences could be attributed to decomposition of the MAX phase powders during the sintering process and in the case of the foams, they could also arise due to reaction of the powder with space holder residues. During foam production using a leachable space holder material, incomplete removal of the space holder due to incorrect elimination might cause undesirable phase changes. A complete de-binding process is therefore essential to prevent formation of any undesired phases as result of the reaction between powder and space holder material or binder.

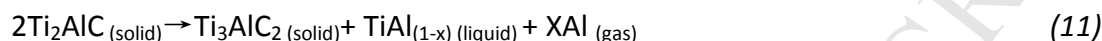
For the  $\text{Ti}_2\text{AlC}$  foams, there are small differences in the phase composition between the samples sintered with and without space holder with respect to the starting powder (Figure 1a and Table 1). These phase changes observed are most probably a result of the higher amount of surface area in the material with space holder, and not a consequence of the reaction of between the  $\text{Ti}_2\text{AlC}$  with and any C from space holder residues. In previous studies on the phase stability of  $\text{Ti}_2\text{AlC}$  foams [17] the phase changes observed were attributed to the sintering cycle. The phase changes observed in this study are consistent



with the phase changes reported in literature for this material during sintering. It can be observed that a higher amount of  $\text{Al}_2\text{O}_3$  phase is present in the material with space holder as a result of oxidation in the foam during sintering, attributed to a higher amount of surface area in the foam. It has been established that at temperatures above  $1400^\circ\text{C}$  in vacuum,  $\text{Ti}_2\text{AlC}$  is susceptible to decomposition through sublimation of Al and Ti to form TiC by the following reaction [41,42]:

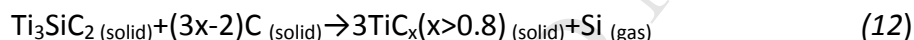


Since sintering was performed in vacuum and the surface area of the foam material is bigger than the material without space holder, this probably accounts for the higher amount of TiC and  $\text{Al}_2\text{O}_3$  observed, as opposed to the material sintered without space holder. In addition, an increase in the amount of  $\text{Ti}_3\text{AlC}_2$  is observed in both samples sintered with and without space holder. It has been reported that  $\text{Ti}_2\text{AlC}$  can transform to  $\text{Ti}_3\text{AlC}_2$  at high temperatures probably through the following reaction [43]:



The amount of  $\text{TiAl}_{(1-x)}$  is almost impossible to detect by x-ray diffraction due to its nonstoichiometry and small amount [43].

Regarding the phase transformations observed in the  $\text{Ti}_3\text{SiC}_2$  foams, previous studies on the phase stability of  $\text{Ti}_3\text{SiC}_2$  reported that  $\text{Ti}_3\text{SiC}_2$  can decompose starting from  $1000$  to  $1400^\circ\text{C}$  in vacuum [44–48]. However, El-Raghy and Barsoum [49] showed that  $\text{Ti}_3\text{SiC}_2$  was thermodynamically stable up to  $1600^\circ\text{C}$  in vacuum furnace for 24 hours. The decomposition at lower temperatures can be caused by small amount of impurities in the starting powder [50]. Previous studies have reported that carbon impurities in porous samples led to the formation of  $\text{TiC}_x$  and vaporization of Si according to the following reaction [51]:



In order to verify that the decomposition of the  $\text{Ti}_3\text{SiC}_2$  occurs partly due to vaporization of Si according to reaction 12, the mass loss during sintering was measured (Figure 2). For the sample without space holder there is a total mass loss of about 3.69 %, including the mass loss due to de-binding of the pressing lubricant, which is 2%. The mass loss during sintering suggests that the vaporization did indeed occur during sintering, regardless of the presence of space holder. The mass loss increases with porosity since the increasing specific surface area favors the removal of Si vapor. This result is consistent with that reported by El Raghy and Barsoum [51]. For the samples with 0% and 60% space holder, the measured molar percentages of TiC after sintering was 21% and 37%, respectively (Table 2). This means that no phase changes are observed for 0% of space holder, whereas a 16% increase in TiC molar percentage for 60% space holder samples is noted. Assuming that all measured mass loss is due to the Si vaporization according to equation 12, the hypothetical increment in TiC phase was calculated for the samples with 0% and 60% of space holder and compared with the observed TiC molar percentage. Comparing the measured mass loss with the increment in TiC phase there was a good agreement with only a difference of 1% and 2% in TiC amount for samples with 0% and 60% of space holder, respectively. This suggests that the mass loss and phase changes are due to the Si evaporation according to reaction 12. Moreover, the amount of C necessary for a 16% increase in TiC molar percentage according to reaction 12 is 125% larger than the total C present in the space holder used and three orders of magnitude larger than any residual C in the sample. Hence, the reaction of  $\text{Ti}_3\text{SiC}_2$  with C to form TiC according to equation 12 is most likely not the only mechanism responsible for the phase changes observed. Therefore, the phase changes are more likely due to the Si vaporization

## 5.2 Effect of porosity on elastic properties

In the present study elastic properties were determined for samples with porosity ranging from 10vol% to 71vol% for  $\text{Ti}_2\text{AlC}$  and 30vol% to 69 vol% for  $\text{Ti}_3\text{SiC}_2$ . To the best of our knowledge, no measurements of the elastic properties were reported before for porosity values higher than 40.5 vol.% for  $\text{Ti}_2\text{AlC}$  and 55 vol.% for  $\text{Ti}_3\text{SiC}_2$ . Four different models have been fitted to the experimental data, namely exponential [30,31], Hasselman [32], CSM [33–35] and the percolation [36–38] Models. Fitting of elastic properties of porous materials over a wider range of porosities with a single equation is usually challenging since an increase in porosity is often accompanied by a change in microstructure or type and shape of pores, for example a change from closed to open porosity as porosity increases. Different fitting models usually are derived assuming specific microstructural characteristics and therefore cannot be used to describe accurately change in elastic properties in a wide porosity range if it is accompanied by changes in the microstructure. All above mentioned existing models are developed for porosity up to approximately 38 vol.% [52].

The exponential model has been cited extensively for predicting elastic properties of porous materials; however, it is an empirical model that fails to satisfy the boundary condition that the Young's modulus must be equal to zero when porosity is 100 vol.%. In addition, this model is only accurate for a narrow range of porosities, i.e., lower than 20 vol.%. Hasselman model is based on the assumption that a continuous phase contains a dispersed phase of spherical particles – in this case dispersed phase consist of pores and thus the elastic properties of the pores are considered to be equal to zero. This model satisfies the boundary conditions and can be used for a wider range of porosities. The CSM considers an assembly of hollow spheres, of different diameters but the same porosity fraction of each cluster of hollow spheres, using the principle of statistical continuum mechanics. The percolation model is based on the percolation theory and the material constant  $a$  is the percolation threshold. Therefore, the minimum value of  $a$  is  $a \geq 1$  for a maximum porosity of 100 vol.%. The percolation threshold is a function of powder size, shape and distribution [36–38].

For  $\text{Ti}_2\text{AlC}$  the model that fits better with the experimental data is the CSM model, has the slightly higher coefficient of determination,  $R^2$ , for both Young's and shear moduli (Table 3). CSM model assumes that the material is isotropic with homogeneous distribution of porosity, which coincides with the main observed microstructural features of the foams. Regardless of that, taking into account that  $R^2$  for Young's and shear moduli (Table 3) varies between 0.89-0.90 and 0.91-0.93, respectively, one can conclude that all four models can be used equally well to describe changes of elastic properties with porosity. The values for  $E_0$  given by the models are slightly lower in all cases than the experimental values for the dense material (277.6 GPa [7]), whereas the values for  $G_0$  are very close to the experimentally measured values (118.8 GPa [29]). The percolation model for the Young's modulus gives a value for the constant  $a$  of 1.1, which corresponds to a percolation threshold value of  $P_c=0.91$ . Therefore, for a porosity of 91 vol%, the Young's modulus should reach zero according to that model. The elastic properties from literature for porous  $\text{Ti}_2\text{AlC}$  are also in good agreement with results presented in this study [7,15,39] (Figure 7).

For  $\text{Ti}_3\text{SiC}_2$ , all models present a good fit of experimental data with values for the coefficient of determination,  $R^2$  exceeding 0.97, Table 4. All  $\text{Ti}_3\text{SiC}_2$  foams have an open cell structure (Figure 3 e-g), and thus the description of the variation of the elastic properties over the whole porosity range with a single equation is more reasonable as there is no change in the type of porosity and foam morphology. The values for  $E_0$  given by the all models are close to

the experimental values for the fully dense material of 343 GPa [29]. Similarly, for all models the values for  $G_0$  are also very close to the experimentally measured value of 143.8 GPa [29] for fully dense samples. The value of the constant  $a$  in the percolation model is 1 and that implies that the elastic constants become zero for a porosity of 100 vol%. Data from Fraczkiewicz [20] follow a similar trend in comparison to the experimental data obtained in this study (Figure 8).

For  $\text{Ti}_2\text{AlC}$  (Figure 9), higher values of  $E$ ,  $G$  and  $B$  are achieved for bigger space holder sizes for porosities in the range of 0-25 vol.%. Examining the type of cell structure for this porosity range (Figure 3 a-c), we found that for bigger space holder sizes, foams with low porosity up to 25 vol.% have mainly a closed cell structure. It is well established that the linear elastic behavior of porous solids depends largely on whether the cells are open or closed [24]. If the cell walls are relatively thin, elastic moduli of closed cell porous structures are identical to those of an open cell foam. However, if this is not the case, the cell edges can strengthen the structure due to the limited deformation mechanisms compared to the open structure, resulting in more rigid structures and higher  $E$ ,  $G$  and  $B$  values. As porosity increases, the differences in the elastic properties for foams with different pore sizes become less significant. For larger porosity values, cell structure is mostly open for all pore sizes, hence the deformation mechanism is similar for all foams, regardless of pore sizes. For  $\text{Ti}_3\text{SiC}_2$ , all the foams in this study had an open cell structure (Figure 3 e-g). Therefore, the rigidity/elasticity of the structure is not altered significantly with increasing porosity. Figure 10 shows no significant differences in the elastic properties for different space holder size ranges.

Microstructural observation of the foams (Figure 4) reveals that they are characterized both by microporosity and macroporosity. The powder particles have angular shape, with high specific surface and with a relative narrow powder particle size distribution. Powders with such characteristic generate a bimodal porosity after sintering: micro-sized pores in the cell walls of the structure (microporosity) and macro-pores (macroporosity) generated by the removal of the space holder.

$\text{Ti}_2\text{AlC}$  samples without space holder have 10% porosity, and this porosity is mainly closed.  $\text{Ti}_3\text{SiC}_2$  samples without space holder show around 31% porosity, which is mostly open. In both cases, the micro-sized pores are present when no space holder is introduced because of incomplete sintering. The average size of the microporosity, estimated using the equivalent circular diameter (ECD) is 1.2-1.8  $\mu\text{m}$  for the  $\text{Ti}_2\text{AlC}$  and 1.3-1.5  $\mu\text{m}$  for the  $\text{Ti}_3\text{SiC}_2$  (Figure 5). As it is evident in Figure 5, the size of the ECD of the microporosity is not affected significantly by either the space holder amount (Figure 5a) or the space holder size distribution (Figure 5b). This later confirms that micro-porosity is result of incomplete sintering of the stuts in the MAX phase foams.

On the other hand, from Figure 6 it can be seen that the amount of microporosity decreases almost linearly with increasing amount of space holder for both materials, whereas the amount of macroporosity increases. This is because microporosity is present only in the cell walls, and thus the relative contribution to porosity from cell walls decreases as the overall porosity increases. In addition, when considering the amount of open and closed porosities, it can be observed that the amount of open porosity increases with increasing amount of space holder regardless of space holder size distribution (Figure 3). These results suggest that as the overall porosity increases, regardless of pore size, the cell walls become thinner and the microporosity becomes interconnected and contributes to the total amount of open porosity. However, the type of porosity, in terms of open or closed porosity, has a more significant influence on the elastic properties than the presence and amount of microporosity, or the size of macro-pores.

Figure 11 presents the experimental results of Poisson's ratio with respect to porosity for both materials in comparison to the literature values [6,15,29,40] from different methods. The differences of the values obtained for each porosity percentage are considerable, and thus it is difficult to establish a trend. The pore shape is strongly linked with the processing technique and some authors have linked changes in Poisson's ratio to changes in microstructure [53–55]. However, results of this study suggest that, in general, increase in porosity can cause the reduction of Poisson's ratio.

## Conclusions

In this study  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  foams have been processed successfully with controlled porosity and pore size using crystalline sugar powder as a space holder. This study shows that:

- The processing method employed can be reliably used to produce  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  with acceptable phase stability. There are small variations in the phase composition of  $\text{Ti}_2\text{AlC}$  foams after sintering samples with and without space holder. For  $\text{Ti}_3\text{SiC}_2$ , decomposition of  $\text{Ti}_3\text{SiC}_2$  into  $\text{TiC}$  is observed during sintering, which is more pronounced with increasing porosity. Mass loss measurements suggest that the phase changes are due to the increase in the specific surface area, which favors Si vaporization. In the case of  $\text{Ti}_2\text{AlC}$ , increase in the amount of  $\text{TiC}$ ,  $\text{Ti}_3\text{AlC}_2$  and  $\text{Al}_2\text{O}_3$  impurities after sintering are noticed and they were attributed to the partial decomposition of  $\text{Ti}_2\text{AlC}$  due to Al vaporization and some additional oxidation of the samples.
- The amount and type of porosity in the foams produced is consistent and can be controlled. The pore size distribution after sintering was found to be bimodal with micro-sized pores (microporosity) and macroporosity. The microporosity is confined to the cell walls and is due to incomplete densification during sintering. The macroporosity results from the removal of space holder. Increasing the amount of space holder leads to increasing macroporosity. As the total amount of porosity increases, regardless of pore size, the cell walls become thinner and the micro-sized pores become interconnected and contribute to the open porosity. Neither the space holder amount nor the space holder size distribution affect significantly the size (EDC) of micro-sized pores.
- Elastic properties were determined for porosity values up to 71 vol% for  $\text{Ti}_2\text{AlC}$  and 69 vol% for  $\text{Ti}_3\text{SiC}_2$ . The exponential model, Hasselman model and CSM model were fitted to the experimental data over the whole range of porosity.
- For  $\text{Ti}_2\text{AlC}$  foams, the variations of Young's and shear moduli with porosity depend mostly on whether the porosity is open or closed. The model that best describes the elastic properties of  $\text{Ti}_2\text{AlC}$  foams over the whole range of porosity is the CSM.
- For  $\text{Ti}_3\text{SiC}_2$  foams, a good fitting of the experimental data of Young's and shear moduli with all the models was obtained over the entire range of porosity.
- Poisson's ratio decreases with increasing porosity for both materials.
- The Young's, bulk and shear moduli were determined for foams with different pore size ranges for both  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$  foams. Porosity type in terms of open or closed porosity has a stronger influence on elastic properties than pore size distribution for both foam materials.

## Acknowledgments

The authors would like to thank the funding provided for this research by the Regional Government of Madrid (Dir. Gral. Universidades e Investigación) through the project S2013/MIT-2862 (MULTIMAT-CHALLENGE-CM), the Spanish Government through the Ramón y Cajal contract RYC-2014-15014 and the project MAT2012-38650-C02-01, the Institute Alvaro Alonso Barba (IAAB) for funding for the research stay in Texas A&M University, and to United States of America - National Science Foundation through grants NSF-CMMI 1233792 and NSF-CMMI 1729350.

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**Highlights:**

- Influence of pore amount and size on elastic properties of MAX foams was evaluated
- Pore size distribution does not affect elastic properties of macro-porous MAX foams.
- Porosity type (open/closed) has stronger influence on elastic properties.
- Existing models were fitted to data and parameters were related to microstructure