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MAX phase Ti_2AlC foams using a leachable space-holder material

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ABSTRACT

MAX phase foams from commercial Ti_2AlC powder were prepared by a ~~novel~~ powder processing method using raw sugar as space-holder. Manufacturing MAX phase foams using this method involves mixing Ti_2AlC powder with raw sugar, pressing the mixture to form a green body followed by space-holder removal and sintering. Green bodies were formed using cold uniaxial pressing and porosity was controlled varying the size and amount of the raw sugar space-holder. Three different space-holder particles sizes in the range of 250-1000 µm and four different volume amounts (20%, 40%, 60% and 80%) of space-holder were studied. The foams produced were characterized, and the size distribution and amount of resulting porosity was compared with the theoretically expected values. Optimal conditions using this ~~novel~~ processing technique for this material were established aiming towards controlling the final microstructures and properties, of porous Ti_2AlC MAX phase.

Keywords

MAX phases, Ti_2AlC, porous materials, eco-friendly processing, water-soluble space-holder

1 Introduction

Ti_2AlC belongs to a group ternary compounds referred to as $M_{n+1}AX_n$ phases or MAX phases, where M is transition metal, A is a IIA or IVA element and X is C or N, n=1,2 or 3 [1]. MAX phases, due to their nanolaminate structure, exhibit unique properties that combine characteristics common to metals such as good thermal and electrical conductivity, good machinability, and damage tolerance with ceramic properties such as high elastic modulus, thermal shock resistance, excellent corrosion /oxidation resistance and self healing capabilities at high temperature [2,3]. Among the more than 70 MAX phases reported so far, Ti_2AlC is the most light-weight (density of 4.11 g/cm^3 [1]) and oxidation resistant [4-9], it has good thermal (46 W/mK [10]) and electrical (2,78 $\mu\Omega^{-1}\,m^{-1}$ [2]) conductivity making it a good candidate for many high-temperature applications such as gas burner nozzles, heating elements and high temperature electrodes [2].

So far the majority of studies reported on this material are on fully dense material. The unique characteristics of MAX phase materials make them ideal for high performance applications which require high efficiency and low weight components capable to work in extreme conditions such as diesel particle filters, heat exchangers, solar volumetric collectors, catalyst substrates and impact-resistant structures. For this kind of applications, porous micro and macrocellular structures become part of the original component design providing added value and high performance. However, only a few recent studies have focused on porous Ti_2AlC [11-19], including some studies on MAX phases/Mg composites fabricated by melt infiltration of porous MAX phase performs [20-22], with exceptional mechanical damping capabilities. In these studies the methods used have been: incomplete densification during sintering or reactive sintering [11-17, 20, 21], replica method using polyurethane foams [23], and the use of NaCl as space-holder [18-19]. Space-holder method produces open and closed porosity by addition of space holder or pore former. Size and shape of the pores are controlled through the morphology characteristics of the space-holder and the amount of porosity is controlled by the metal/powder volume ratio [24]. Elimination of some space-holders is performed by heating at high temperature. This step can result in gas formation during sintering that can lead to cracks in the foam. Leachable space-holder, such as NaCl, permits an easy elimination by dissolution in water before sintering and avoids gas formation during sintering. This method has been studied and good results have been reported for many alloys [25]. NaCl has been employed to make Ti_2AlC foams, however pore shape became elliptical and oriented, rather than the cubic–like shape of NaCl particles, as a consequence of deformation of the particles during cold press loading [18]. Foams have also been produced employing crystalline carbohydrate as a space-holder and soaking in water under controlled conditions before sintering [26-33], however, MAX phase foams have not been previously produced using this method. These studies have reported that employing sugar as space holder the internal architecture of the foam is controlled as well as porosities and pore size.

Control of porosity allows tailoring of mechanical and functional properties, and several studies reveal that porous MAX phases have potential applications as: supports for highly efficient catalytic devices [23,34] or MAX phases/Mg composites for mechanical dumping [14,21,22]. Porous Ti_2AlC presents potential applications as solar volumetric collectors because of its combination of good corrosion and oxidation resistance and good mechanical properties at high temperature [1-3].

In this study a simple and inexpensive space-holder method for manufacturing Ti_2AlC foams is reported using crystalline carbohydrate (sugar) particles as a leachable agent. Weight measurements were performed to determine the extent of space-holder removal. The cell morphology and porosity of produced foams was characterized.

2 Materials and Methods

Ti_2AlC powder was provided by Sandvik (Sweden). The powder´s average particle size was characterized using a Mastersizer 2000 equipment (D_{50}=9 µm), the specific surface area using BET (2,7674 m^2/g) and the density of the powder was determined using a helium pycnometer Accupyc (4,122 g/cm^3). The phase constitution of the powder and sintered material was determined by X-ray diffraction resulting in two major phases: Ti_2AlC (ICSD: 165460) and Ti_3AlC_2 (ICSD: 153266), and minor phases: Al_2O_3 (ICSD: 10425) and TiC (ICSD: 44495). The powder was mixed with 2% of acrowax C ($C_{38}H_{76}N_2O_2$) (Lonza) atomized lubricant to facilitate the pressing step. The space-holder used was commercial raw sugar, in three size distributions: 250-400 µm, 400-800 µm and 800-1000 µm that were obtained by sieving the raw sugar. The particle size distribution in each of the three ranges was measured after sieving using a Mastersizer 2000 equipment and is given in Table 1. The powder and the space-holder were mixed in a Turbula® mixer for 1 hour. Four different fractions of space-holder were used: 20%, 40%, 60% and 80% in volume. Blends were pressed in a uniaxial cylindrical die (16 mm in diameter) at 800 MPa obtaining the green body. The space-holder was dissolved prior to sintering by soaking in water, during 12 hours at 60 °C. Then the samples were dried during 24 hours at 30 °C. To control sugar elimination two verifications were performed: a) mass loss, where the green body mass was measured before and after space-holder dissolution and was compared to the expected mass loss for complete sugar removal, considering the vol % of space-holder added and b) chemical analysis, using LECO-CS200 equipment, where the weight % of carbon present in the sintered foams was compared to the C content present in the powder prior to blending as well as to the C in the sintered samples without space-holder. Subsequently, the sintering was performed in vacuum (10^{-5} mbar) at 1400 °C during 4 hours including a 30 min dwell at 400 °C for delubrication purposes. Shrinkage of the samples due to sintering was measured by standard dimension measurement of the samples prior and after sintering using calipers Open, closed and total porosity of foams was estimated as specified by ASTM C20-00 applying the ethanol immersion method based on Archimedes' principle and using the following equations:

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

$$Porosity_{\ Overall}(\%) = \left(1 - \frac{\rho}{\rho_{teorethical}}\right) \cdot 100 \qquad (2)$$

$$Porosity_{open}\,(\%) = \left(\frac{wet\ mass - dry\ mass}{wet\ mass - suspended\ mass}\right) \cdot 100 \tag{3}$$

$$Porosity_{closed}(\%) = Porosity_{Overall}\,(\%) - Porosity_{open}\,(\%) \tag{4}$$

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, $\rho_{ethanol}$ is the density (g/cm^3) of ethanol, Porosity$_{overall}$ is the volume fraction of the overall porosity (vol.%) of the sample, Porosity$_{closed}$ is the volume fraction (vol. %) of the closed porosity if the sample and Porosity$_{open}$ is volume fraction of the open porosity of the sample. The theoretical density of the powder, $\rho_{theoretical}$, was determined measuring powder density by helium pycnometer Accupyc.

The cell morphology of foams was characterized using a scanning electron microscopy (SEM) (JEOL-6500F). Metallographic preparation included grinding with SiC abrasive paper and polishing with 1 micron diamond powder. Image analysis was performed by image-J software on SEM images to foams with one amount of space holder (60%) and three different size distributions. Each foam was analyzed using SEM images which where representative of the porosity of the sample. The images were binarized to define the pore area, then the pore size. The average pore size and standard deviation were determined by measuring pore size values as

$$\overline{\mathrm{X}} = \frac{1}{\mathrm{N}}\sum_{\mathrm{i}=1}^{\mathrm{N}} \mathrm{x_i} \tag{5}$$

And

$$\mathrm{s} = \sqrt{\frac{1}{\mathrm{N}}\sum_{\mathrm{i}}^{\mathrm{N}}(\mathrm{x_i} - \overline{\mathrm{x}})^2} \tag{6}$$

respectively, where N is the total number of the pore size values measured from SEM images, $\mathrm{x_i}$ is the pore size value and $\overline{\mathrm{x}}$ is the average pore size value.

3 Results and Discussion

3.1 Space-holder dissolution, phase identification and chemical analysis

The space-holder was eliminated by soaking it in water prior to sintering Figure 1 shows the relative mass loss after soaking with respect to space-holder particle size range for each one of the space-holder volume fractions. A value of 100% corresponds to mass loss equivalent to the total mass of the space-holder present for each of the volume fractions and space-holder size ranges, respectively, hence corresponding to complete space-holder elimination. For smaller space-holder particle sizes the relative mass loss is slightly lower, indicating that it is probably more difficult to eliminate completely the space-holder for smaller space-holder sizes. Nevertheless the relative mass loss approaches values of around 90%, indicating that a relative small amount, if any, of space-holder remains after soaking. Increasing the amount of space-holder in the particle size range of 250-400 μm makes space-holder removal more difficult. However this is not observed for bigger particle size ranges, where no clear tendency of relative mass loss and volume fraction of space-holder is evident. For higher space-holder particle sizes the relative mass loss approaches values of almost 100% indicating almost complete space-holder removal. In some cases values above 100% are observed. Observations during this dissolution process suggest that this is probably due to loss of some MAX-phase powder itself, particularly in the case of higher space-holder particle size. Space-holder elimination is performed on the green body, before sintering and, although this is beneficial because it will allow greater space-holder removal, on the other hand, at this stage, after cold pressing there is no diffusional bonding in-between particles therefore particle bonding is relatively weak, allowing for some powder loss during this dissolution process.

Figure 2 shows the XRD spectrum plotted in terms of relative intensity for the raw powder, the sintered material without space holder and two selected, but typical, sample of sintered foams. All samples have the same phases present: two major phases: Ti_2AlC and Ti_3AlC_2, and two minor phases, in small amounts: Al_2O_3 and TiC. The fraction of the different phases present was determined by normalizing the intensity of the highest XRD peaks for each phase and is shown in Table 2. Similar phase constitution for the starting Ti_2AlC powder, provided by this supplier, has been reported before [18]. It has also been reported that during sintering the amount of Ti_3AlC_2 phase increases and the amount of Ti_2AlC decreases, due to de decomposition of Ti_2AlC to Ti_3AlC_2 according to the following reaction [35]

$$2Ti_2AlC_{(s)} \rightarrow Ti_3AlC_{2(s)} + TiAl_{(1-x)} + xAl_{\ (g\ or\ l)} \qquad (7)$$

where x≤ 1. Decompositon according to this reaction will be more severe in porous samples, as compared to fully dense samples, because of their high surface area, which allows faster loss of Al, due to its vaporization at high temperatures. Ti_3AlC_2 can also be formed by reaction of Ti_2AlC with TiC:

$$Ti_2AlC + TiC \rightarrow Ti_3AlC_2 \qquad (8)$$

If decomposition of Ti_2AlC intoTi_3AlC occurs by reaction with TiC, the amount of decrease of Ti_2AlC should be similar to the amount of the increase of Ti_3AlC, whereas if decomposition occurs without reaction with TiC the amount of decrease of Ti_2AlC should be twice the amount of increase of Ti_3AlC. In this case, for the sample without space holder, the amount of decrease of Ti_2AlC is lower that the amount of increase of Ti_3AlC_2 and in addition the amount of TiC seems to decrease. Similar trend is observed for the foam with 20% of space holder. Therefore decomposition is more likely to be occurring due to reaction with TiC in both cases. This suggests that the phase transformations occurring in the foam are similar to those that occur in the dense material and hence are not affected by any remaining amount of space holder. For higher amount of space holder (40 vol. %) it appears that the amount of Ti_2AlC actually increases. The exact mechanism by which this occurs it is not clear at present, however, this phase stabilization is considered beneficial.

The amount of retained sugar in the foams was also studied by chemical analysis of carbon content (Table 3). The powder used for making the foams contained 2% in weight of acrowax (used as pressing lubricant) and as a consequence contains 1.99 wt % more C than the raw starting powder. The sintered material without space holder shows lower amount of C than the starting powder with acrowax due to the fact that the acrowax lubricatnt is burned at sintering cycle during the 30 min dwell step at 400ºC so after sintering the % wt of C decreases. However, the amount of C for sintered material without space holder is still higher than the raw starting powder. This is attributed to mass loss during sintering, specifically to loss of Al, even possibly some Ti, that can both vaporize at high temperature and go to the surroundings. A mass loss of around 5 % was measured after sintering for the materials without space holder, and higher amounts up to 8 wt% was observed for porous samples that show higher mass loss due to higher surface area. Reports of mass loss for this type of material during sintering have been previously reported [18]. Sintered foams exhibit values close to sintered material without space-holder and to the theoretical content in Ti_2AlC and variations of carbon contents in foams after dissolution are low. Therefore in can be concluded that overall dissolution process is successful, no addition C is introduced due to the presence of the space holder and phase transformations occurring in the foams are similar to those that would occur in the starting powder due to sintering.

3.2. Characterization of porosity, pore morphology and foam microstructure

Porosity was quantitatively characterized by determination of open, closed and total porosity. Figure 3 shows the variation of porosity with the volume fraction of space-holder for different sizes of space-holder. All the samples were compared to the sintered material without space-holder which was pressed and sintered under the same conditions as the foams but without any space-holder. For all foams most of the porosity appears to be open porosity (interconnected). Closed porosity remains relatively stable with the increase in space-holder volume percentage, and this effect is emphasized with the increase in the size of space-holder. On the contrary, open porosity increases with space-holder volume percentage, regardless of space-holder size. Therefore it appears that most of the porosity due to the addition of space-holders is open interconnected porosity. Closed porosity may be due to an incomplete densification during sintering.

Porosity obtained experimentally does not match up the theoretical expected porosity due to amount of space-holder added (Figure 3d). The total porosity percentage is higher than the space-holder volume up to 40% volume faction of space-holder added. This confirms that part of the porosity present is also partially a result of incomplete sintering. From 40% up to 80% vol. space-holder, total porosity is lower than theoretical porosity. During the elimination of the space-holder mass loss occurred due to the dissolution of the space-holder as well as removal of some powder, as already mentioned. This could lead to a modification in the structure decreasing the total porosity.

Porosity was also characterized by image analysis on foams with 60% vol. of space holder with three size distributions: 250-400 μm, 400-800 μm and 800-1000 μm (Figure 4). The range of particle size distribution measured form image analysis is in agreement with the space holder particle size for smaller space holder particle size (250-400 μm). For the intermediate (400-800 μm) space holder size distribution it appears that most of the pores (about 60 %) are above 500μm in size, whereas there is also a considerable fraction of pores (about 25%) with sizes smaller than 400 μm. Similarly, for the particle biggest space holder size distribution (800-1000 μm) there is a constant distribution for pore sizes above about 500 μm in size, however there is a considerable fraction of pores with sizes smaller than 500 μm, outside the range of the space holder initial size.

The average pore size and standard deviation obtained from image analysis is presented on Table 4. The particle size measured by image analysis is compared to the average space holder size for each one of the space holder size ranges. The average space holder size for each one of the space holder size ranges was measured prior to foam production (Table 1), however, during sintering some shrinkage occurs which will modify the expected pore size. The expected average space holder pore size considering the shrinkage observed experimentally during sintering is also presented in Table 4. For this calculation it was assumed that shrinkage occurs homogeneously. For all space holder particle size ranges the measured average pore size is smaller than the expected pore size due to space holder size, even after considering the shrinkage. This is especially the case for larger space holder size range (800-1000μm), where there are also a considerable number of pores with sizes outside the range of the initial space holder size, which could be a result of collapsing of bigger pores. These results indicate final average pore size will, in general, be smaller than the initial space holder size, especially for larger space holder size. This is probably both due to shrinkage during sintering as well as bigger pores spiting into smaller ones.

Figure 5 shows SEM images of the foams obtained for different space-holder sizes and volume fractions. Pore morphology is not directional and pores are relatively homogeneous and randomly distributed. When volume percentage of space-holder increases, the percentage of porosity and homogeneity in porosity increases. If the space-holder amount increases, the possibility of space-holder particles touching increases producing interconnected pores. Previous studies with leachable space holders show that with increasing amount of space holder, pores become more elliptical and oriented as a consequence of crushing during cold press loading [18]. It is worth nothing that this effect is not observed in this case, even for 80% volume of space holder.

The microstructure of the foams was examined in more detail using backscatter electron microscopy and EDX. Figure 6 shows a representative image of microstructure of the necks, or dense regions, in between the pores at high magnification. Two phases can be observed: 1) one main the matrix phases with darker color and 2) another minor in a lighter color. In addition, microporosity is clearly visible in this region, confirming the porosity measurement results that indicated a large amount of closed porosity is present due to incomplete sintering. Table 5 shows the results of the EDX analysis realized on the two phases observed. The stoichiometric relationship between Ti, Al and C on the main matrix phase confirm that his corresponds to the Ti_2AlC, as confirmed by XRD, whereas the lightest most probably corresponds to Ti_3AlC_2. The minor phases, Al_2O_3, and TiC, detected by XRD were observed, neither on the foams or compared the material without space holder. It is possible lighter phase, or part of it, might also correspond to TiC phase, since the difference in contrast between TiC and Ti_3AlC_2 in backscattered electron image might not be sufficient to differentiate between the two. In addition, this phase is considerably narrower than the matrix, so the EDX analysis is less accurate, taking information from the elements contained in neighboring area (Ti_2AlC). These results are in agreement with the XRD phase identification. In general the microstructure of the obtained foams is consistent with the expected for this material.

4 Conclusions

A simple, economic and environmentally friendly process was employed to make porous Ti_2AlC foams employing raw sugar as space-holder with controlled porosity amount and size. Mass loss measurement after space holder dissolution, C chemical analysis and phase identification confirm successful removal of leachable space holder. The overall, open and closed porosity and distribution was characterized. Foams with homogenous porosity ranging from 23 vol% to 76 vol% where successfully produced. Differences were found between experimental and expected porosity. For space-holder addition lower than 40% in volume, experimental porosity is higher than expected and the opposite occurs for space-holder additions higher than 40%. Differences between expected and experimental porosity are due to a combined effect of incomplete sintering and material loss during space-holder dissolution. Average pore size in the produced foams is in general smaller than the initial space holder size, as a result of sintering, and this is more pronounced for bigger space holder sizes. Phase evolution during sintering shows partial decomposition of Ti_2AlC into Ti_3AlC_2.

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Table 1. Space holder size distribution for each space holder size range.

Space holder range (µm)	**D_{10} (µm)**	**D_{50} (µm)**	**D_{90} (µm)**
250-400	259	385	571
400-800	448	640	924
800-1000	696	1015	1466

Table 2. Fraction of the phases present in the starting Ti_2AlC powder, sintered Ti_2AlC sample and porous Ti_2AlC foams as determined by relative intensity of the highest peaks of each phase.

Sample	**Fraction of Phases**			
	Ti_2AlC	**Ti_3AlC_2**	**Al_2O_3**	**TiC**
Starting Ti_2AlC Powder	67.9	25.0	4.3	2.9
Sample with 0 vol.% space holder	61.0	37.2	1.2	0.6
Foam with 20 vol.% space holder (250-400 μm)	63.7	32.5	2.5	1.3
Foam with 40 vol.% space holder (250-400 μm)	75.8	21.2	1.5	1.5

Table 3. Chemical analysis of carbon content in starting powder, sintered sample without space-holder and sintered foams with space holder particle size distribution of 800-1000µm and different volume of space holder. The theoretical value in powder was calculated as the theoretical % wt C contained in stoichiometric Ti_2AlC.

% wt C							
Theoretical content in Ti_2AlC	**Powder**		**Sintered Foams**				
	Starting Powder	**Powder + 2% acrowax**	Volume percentage of space holder (size range 800-1000 µm)				
			0%	**20% vol.**	**40% vol.**	**60% vol.**	**80% vol.**
8.91	7.86	9.85	8.42	9.09	9.62	9.60	9.58

Table 4. Comparison between average pore size measured by image analysis and space holder size for three space holder size ranges. Space holder average size, D_{50}, corresponds to the average size of the size distribution measured with particle size analysis. The space holder average size after shrinkage corresponds to the average size of the spaces holder minus the shrinkage (%) experimentally measured for each space holder size range.

Average pore size (µm)	**Space holder range (µm)**	**Space holder average size D_{50} (µm)**	**Space holder average size after shrinkage (µm)**
229 ± 97	250-400	385	368
478 ± 157	400-800	640	609
513 ± 166	800-1000	1015	962

Table 5. EDX analysis of sintered sample without space holder and sintered foams with the same space holder size distribution (250-400) µm and different space holder % in volume (20%, 40%, 60% and 80%) and with the same space holder volume (60%) and different space holder size distribution (250-400 µm, 400-800 µm, 800-1000 µm).

Sample	**Dark area (At %) (1)**			**Light area (At %) (2)**		
	Ti	**Al**	**C**	**Ti**	**Al**	**C**
Without Space holder	48	24	28	51	17	32
20%vol. (250-400) µm Space holder	53	23	24	57	27	16
40%vol. (250-400) µm Space holder	51	26	23	60	7	33
60%vol. (250-400) µm Space holder	51	27	22	58	11	31
80%vol. (250-400) µm Space holder	51	27	22	55	7	38
60%vol. (400-800) µm Space holder	56	29	15	60	6	34
60%vol. (800-1000) µm Space holder	51	27	22	67	1	32

Figure Captions

Figure 1. Relative mass loss after soaking in water for different space-holder size distributions and their percent volume fraction.

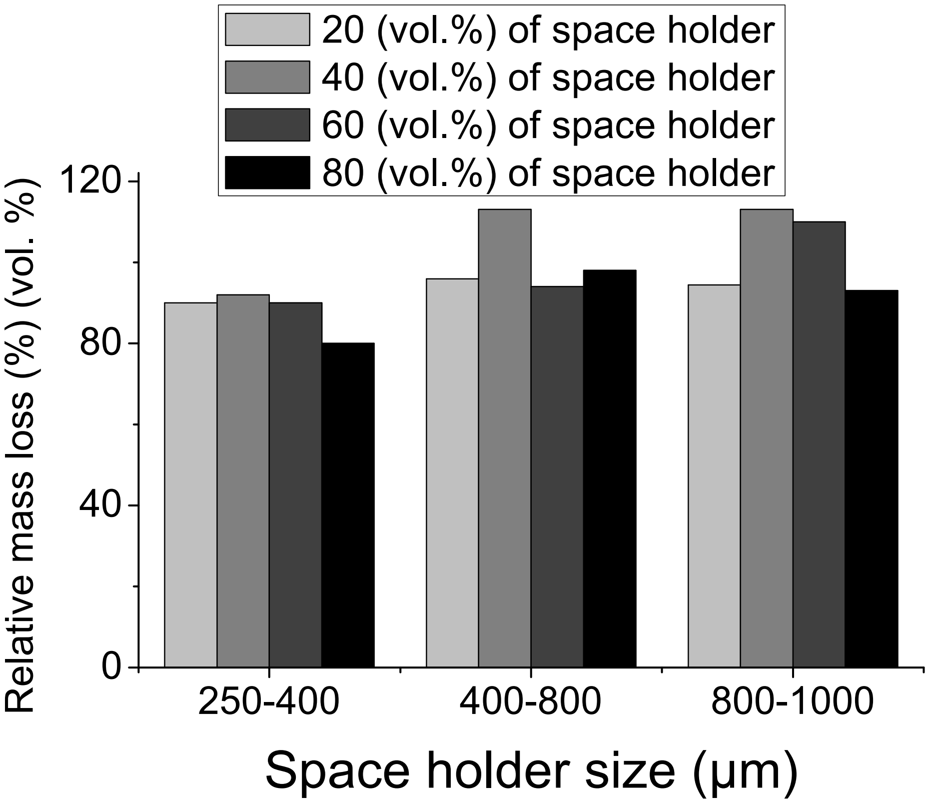
Figure 2. XRD of starting Ti_2AlC powder, sintered material without space holder and Ti_2AlC foams with 250-400 µm size distribution and different % in vol of space holder: 20% and 40 %.The phases identification was according to the Inorganic Crystal Structure Database (ICSD) collection code 165460 for Ti_2AlC, 153266 for Ti_3AlC2, 10425 for Al_2O_3 and 44494 for TiC, respectively.

Figure 3. Variation of porosity with the amount of space-holder added for different space-holder size distributions (a) 250-400 µm, (b) 400-800 µm and (c) 800-1000 µm. (d) Total porosity variation with space-holder percentage for different space-holder sizes. The dotted line indicates the theoretical porosity that the foam would have if all its porosity was made by space-holder.

Figure 4. Pore fraction versus pore size for three pore size ranges (250-400 µm, 400-800 µm, 800-1000 µm) and fixed space holder amount (60 vol.%).

Figure 5. Secondary electron microcopy image of a Ti_2AlC foams. With 60% volume percentage of space-holder for three space-holder size distributions: (a) 250-400 µm, (b) 400-800 µm, (c)800-1000 µm. With 250-400 µm space-holder size distribution for three volume space-holder percentages: (d) 20%, (e) 40% and (f) 80 %.

Figure 6. Secondary electron image (Backscattered mode) of foam with 60% volume percentage and space-holder space-holder size distributions of 800-1000 µm. . Two phases are distinguished: 1) matrix phase(darker area) and 2) secondary phase (lighter area)



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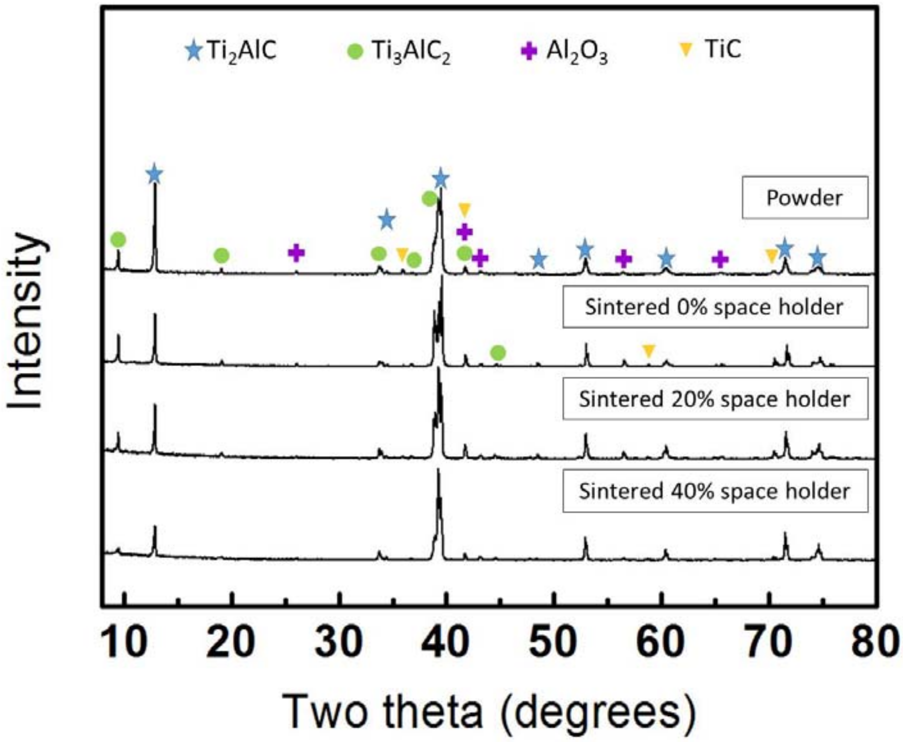

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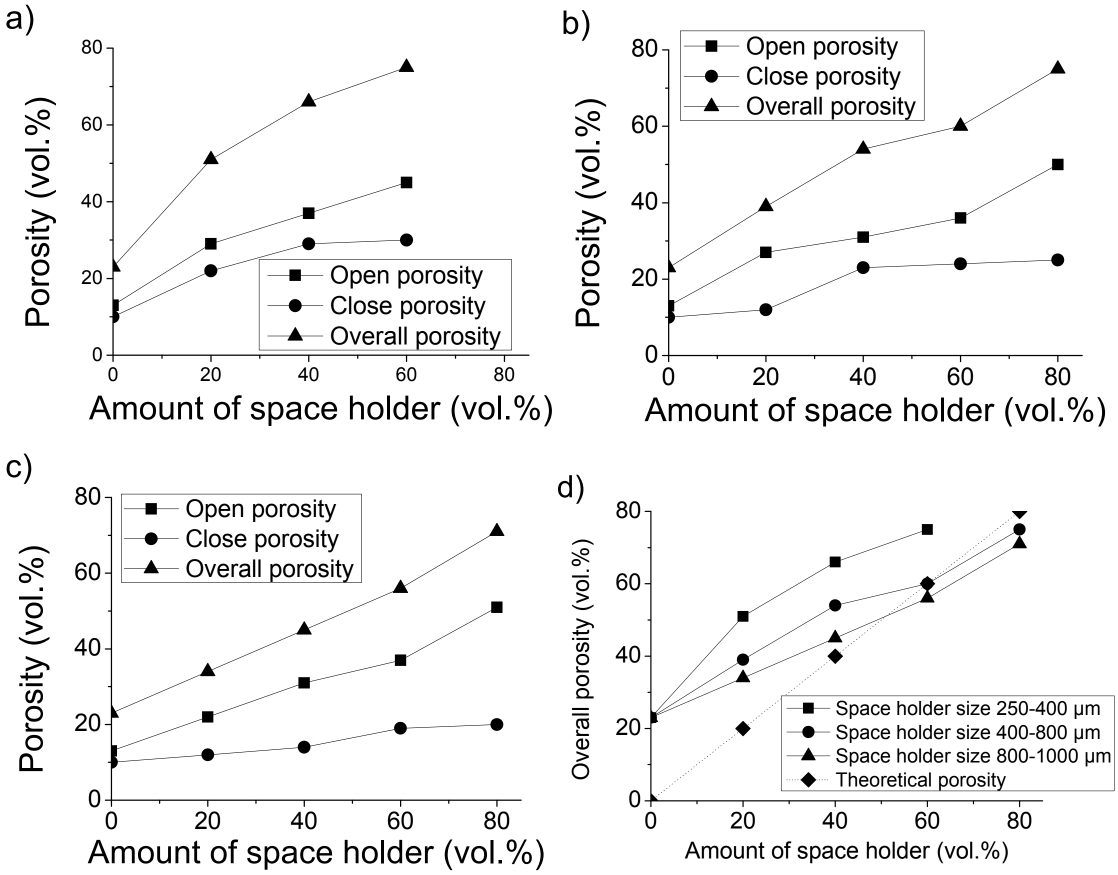

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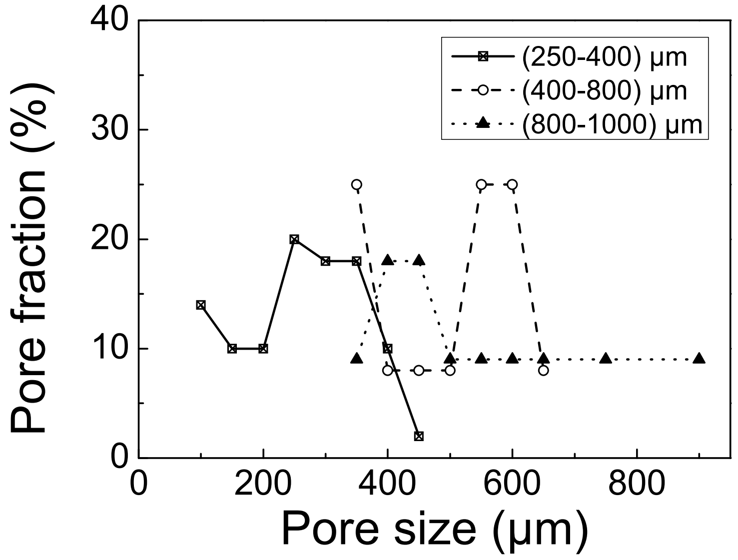
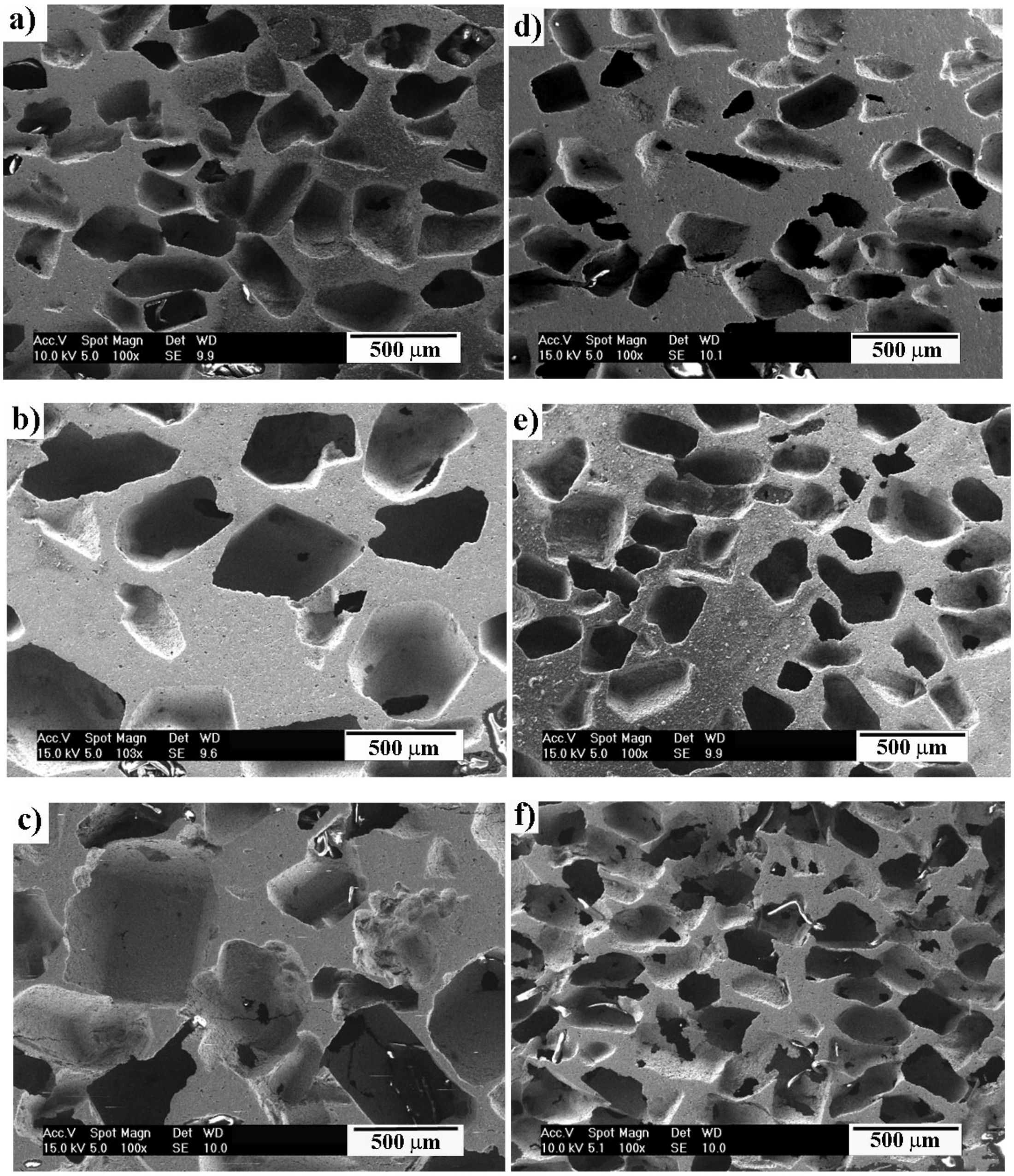


Figure 4. Pore fraction versus pore size for three different size distributions (250-400 µm, 400-800 µm, 800-1000 µm) and fixed space holder amount (60 vol.%).



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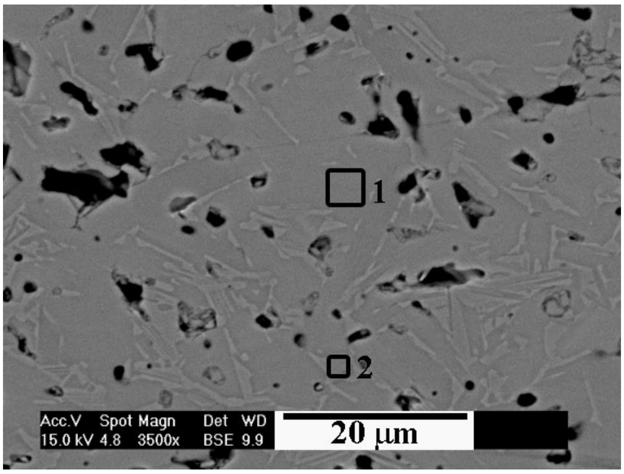

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