Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 1803–1811

www.elsevier.com/locate/jeurceramsoc

Structural investigation of substoichiometry and solid solution effects in $Ti_2Al(C_x,N_{1-x})_y$ compounds

Thierry Cabioc'h*, Per Eklund[a], Vincent Mauchamp, Michel Jaouen

Département de Physique et Mécanique des Matériaux, Institut P' UPR 3346 CNRS - Université de Poitiers - ENSMA, SP2MI, Téléport 2, BP30179, 86962 Futuroscope, France

Received 24 May 2011; received in revised form 30 November 2011; accepted 11 December 2011
Available online 18 January 2012

Abstract

The milling, cold compaction and thermal annealing (4 h–1400 °C–Ar flow) of Ti, TiC, Al and AlN powders were used to produce $Ti_2Al(C_xN_{(1-x)})_y$ compounds with $x = 0$, 0.25, 0.5, 0.75, 1 and $0.7 \le y \le 1$. X-ray diffraction analysis, scanning electron microscopy observations combined with microanalysis confirmed the formation of the almost pure $Ti_2AlC_xN_{(1-x)}$ carbonitrides for $y = 1$ whereas increasing amounts of titanium aluminides were formed when y decreases. Proportions of the different phases deduced from Rietveld refinements of the X-ray diffractograms indicate that no or very poor substoichiometry in carbon was possible in carbide whereas C and N deficiency can be achieved in nitrides and carbonitrides $Ti_2AlC_xN_{(1-x)}$. Electron Energy Loss Spectroscopy investigations confirm that carbonitrides can have at least 20% of vacancies on the C or N site. The a lattice parameter varies linearly with x whereas it is not the case for the c lattice parameter, its values being lower for the carbonitrides. Furthermore, a strong broadening of the carbonitrides' XRD peaks is observed, a phenomenon that can be mainly attributed to C and N concentration gradients inside the samples.

Keywords: Sintering; X-ray methods; Carbides; Nitrides; MAX phase

1. Introduction

The $M_{n+1}AX_n$ phases ($n = 1$–3, or 'MAX phases') are a group of transition metal (M) carbides and nitrides (X) interleaved with an A-group element, with an inherently nanolaminated crystal structure that imparts an exciting combination of ceramic and metallic properties to these phases. Up-to-date exhaustive reviews about these compounds can be found in Refs.[1, 2].

It is well known that it is possible to obtain isostructural MAX phases solid solutions both on M, A, and X-sites.[1] MAX carbonitrides, e.g. $M_{n+1}A(C,N)_n$ phases and in particular $Ti_2Al(C,N)$, are the most important examples of MAX phases solid solutions on the X site. N and C have similar chemical bonding characteristics, resembling those of the binaries TiC and TiN, and consequently one can form a wide range of $Ti_2Al(C,N)$ solid solutions. This is important not only because it allows to understand correlations between chemistry and physical properties, but also because it offers the possibility to tune the properties of these compounds. For example, $Ti_2AlC_{0.5}N_{0.5}$ has been shown[3–5] to be harder and stiffer than Ti_2AlC and Ti_2AlN. In addition to the carbonitrides, it has recently been demonstrated that MAX oxycarbides and oxynitrides, $Ti_2Al(C,O)$ and $Ti_2Al(N,O)$, can be formed, either due to incorporation of oxygen from the residual gas in a vacuum deposition process,[6] or due to a reaction between a TiC, TiN, or Ti_2AlC film with an Al_2O_3 substrate.[7–9] Although pure M_2AX oxides, e.g. Ti_2AlO, are likely unstable, there are theoretical indications that the oxygen saturation content on C sites in $M_{n+1}A(C,O)_n$ solid solutions may be as large as 25–75%.[10]

The general formula $M_{n+1}AX_n$ gives the different MAX stoichiometries as 211 ($n = 1$), 312 ($n = 2$), and 413 ($n = 3$). However, "211", "312", and "413" are not necessarily the exact stoichiometries. It is well documented that the binary carbides and nitrides, which constitute the MX building blocks in the MAX phases, can exist in a wide composition range. TiC, for example, has a single-phase field from $TiC_{0.5}$ to $TiC_{0.98}$[11] and some of its physical properties (e.g. electrical resistivity, thermal

---

* Corresponding author. Tel.: +33 549496769; fax: +33 549496692.
E-mail address: thierry.cabioch@univ-poitiers.fr (T. Cabioc'h).

[a] Permanent address: Thin Film Physics Division, Linköping University, IFM, 581 83 Linköping, Sweden.

0955-2219/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2011.12.011

conductivity)[12,13] strongly vary with the introduction of carbon vacancies. It also exists in a wide range of solid solutions between TiN and TiC. Indeed, Ti(C,N) layers are largely used for cutting tools and wear resistant coatings. Wear resistance improvement and hardness increase of titanium carbonitrides thin films were extensively studied over the last 20 years. Not surprisingly, substoichiometry in C and N can be easily obtained for such carbonitrides.

Substoichiometry of the X component in the MAX phases is therefore expected. Several results in the literature show that Ti_2AlN,[14] Ti_4AlN_3,[15] Ti_3AlC_2,[16] and V_4AlC_3,[17] can be substantially substoichiometric in the X element. From Density Functional Theory (DFT) calculations, it has been predicted that the introduction of N or C vacancies in $Ti_4AlN_{3-\delta}$ and $V_4AlC_{3-\delta}$, respectively, increases the phase stability relative to the stoichiometric 413 phases.[18,19] In contrast, a similar calculation for α-Ta_4AlC_3 suggests that a small amount of C vacancies in Ta_4AlC_3 reduces its stability compared to the stoichiometric structure,[20] and there are no experimental indications that α-Ta_4AlC_3 is understoichiometric in C.[21,22] Nevertheless, there is most likely a stoichiometry range for X-site vacancies for most MAX phases, as for the binary carbides and nitrides.

The combination of X-site substoichiometry in a solid solution is interesting to study from a fundamental point-of-view and also because it is known to affect properties such as hardness and conductivity. While Pietzka and Schuster[23] reported a continuous range of solid solutions in $Ti_2Al(C_x,N_{1-x})_{0.8}$, systematic studies of these effects are essentially lacking. Therefore, in this paper we report on the possibility of having C and/or N vacancies in the $Ti_2Al(C,N)$ compounds by varying systematically the carbon and nitrogen concentrations in reactants and then by considering the products obtained after performing an identical thermal treatment.

2. Experimental details

$Ti_2Al(C_x,N_{1-x})_y$ compounds were synthesized by using conventional powder metallurgy techniques. Commercial Ti, Al, AlN and TiC powders were carefully weighed to obtain the nominal compositions: 2Ti:1.1Al:xyC:$(1-x)y$N. An excess of 10% Al was chosen to compensate the loss of aluminum by evaporation during the sintering process. After 4 h of mixing (Turbula™ shaker), cylindrical compacts, 12 mm in diameter and 3 or 4 g in weight, of the mixed powders were hand pressed (uniaxial cold compaction). The so obtained cylinders present a good green strength and an open porosity of ~40%. Natural reactive sintering of all samples was performed in a furnace (Nabertherm™) maintaining a primary vacuum up to 400 °C to avoid oxygen contamination. A constant argon flow was then applied for higher temperatures till the end of the thermal procedure which consisted in maintaining the samples at 1400 °C for 4 h. The porosity and the true density of the so obtained samples were measured by using Archimedes' law and Helium picnometry. One face of the cylindrical samples was mechanically polished prior to further characterizations. X-ray diffraction (XRD) data were obtained on the polished face using the Cu Kα radiation of a Bruker D8 advance diffractometer in the Bragg–Brentano geometry, the divergence and receiving slits being set at 0.02 mm. The selected 2θ range (10–80°) covers most of the intense peaks of $Ti_2AlC_xN_{1-x}$. The instrument was operating at 40 kV and 40 mA. Steps interval of 0.02° or 0.03° (2θ) and counting time varying between 5 and 20 s for each step were used. The pattern of a Cr_2O_3 powder (Standard NIST 600) was collected at the same geometrical conditions to generate an instrumental resolution function to account for the experimental broadening. Rietveld refinements of the diffractograms were performed using the Materials Analysis Using Diffraction (MAUD) software.[24]

The polished surfaces of all the samples were also examined in a scanning electron microscope (SEM) (JEOL 5600 LV). Energy Dispersive X-ray (EDX) microanalysis were performed in the SEM to determine the global Ti/Al ratio of the sample; but also that of the different phases observed, at a micrometric scale, on backscattered electrons SEM images. Some samples were prepared for Transmission Electron Microscopy (TEM). The polished surfaces of sintered samples were scratched by a diamond tool to get small amount of powders. These last were hand milled with an agate mortar in an agate crucible to obtain, on the boarder of micrometric grains, areas thin enough for TEM and Electron Energy Loss Spectroscopy (EELS) analysis. TEM-EELS experiments were performed in a JEOL 2200-FS operating at 200 kV equipped with an in-column omega filter. Spectra were dark count corrected and deconvoluted from multiple scattering using a Fourier–Ratio technique. The standard procedure implemented in the Gatan Digital Micrograph software was used to perform the quantification of C/N ratio from the carbon and nitrogen K edges. The error on a single quantification is estimated to be on the order of 10% as confirmed when performing measurements on various grains of the same composition.

3. Results and discussion

3.1. $Ti_2AlC_xN_{(1-x)}$ carbonitrides

Results obtained on $Ti_2AlC_xN_{(1-x)}$ compounds (then after called "stoichiometric compounds" for simplicity to distinguish them from nitrogen- and/or carbon-deficient compounds) are at first described before discussing the results obtained for nitrogen- and/or carbon-deficient compounds. Porosimetry experiments showed that all samples were porous whatever the stoichiometry. If the carbide sample ($x = 1$) exhibits the largest porosity (45%), this last progressively decreases with an increasing nitrogen content down to a value of 32% for the pure nitride ($x = 0$). SEM observations confirm these results, as numerous pores are observed (Fig. 1). In Fig. 1b are evidenced grains, 2–10 μm in size, as well as flat polished sections of dense aggregates. For all samples, EDX showed that the overall Ti/Al ratio is very close to 2. This confirms the expected loss of approximately 10% of the aluminum during the reactive sintering of the samples. No oxygen was detected whereas Kα lines from C and N were easily observed, especially on the micrometric grains as those seen in Fig. 1b. In contrast, at the center of

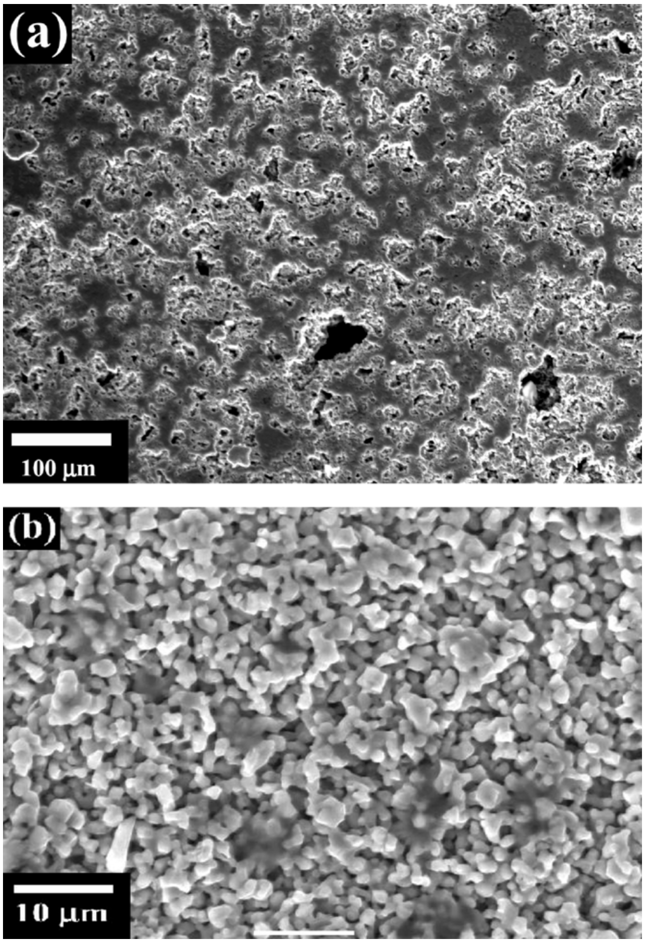

Fig. 1. Typical SEM micrographies (secondary electrons) of a polished section of $Ti_2AlC_xN_{(1-x)}$ samples. Large scale view (a) and higher magnification micrography from an area between denser aggregates (b).

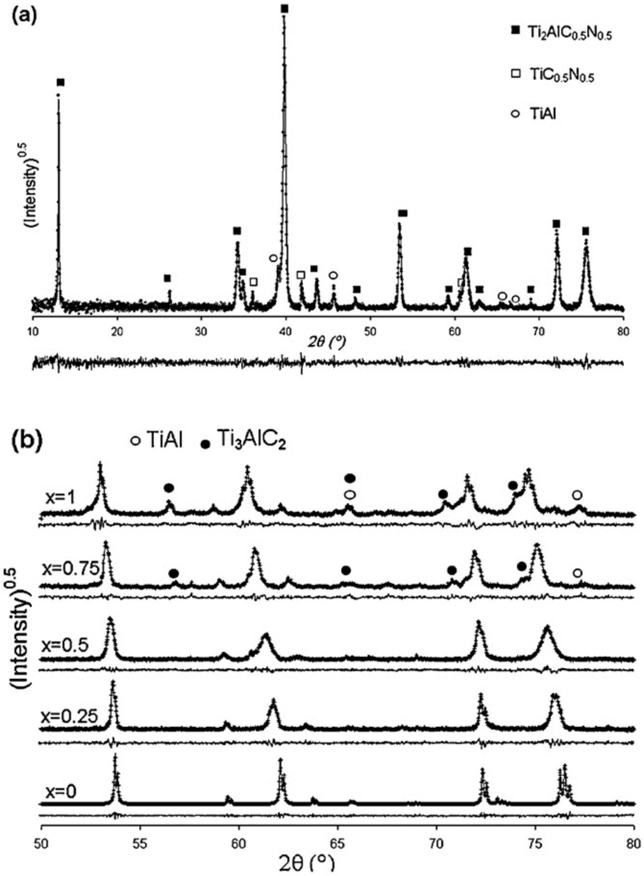

Fig. 2. XRD diffractograms and Rietveld refinements of $Ti_2AlC_xN_{(1-x)}$ compounds. Residual is shown below every diffractogram. (a) Typical XRD diffractogram obtained for the case $x = 0.5$ in the 10–80° 2θ range. (b) Evolution of the XRD diffractograms for various x values in the 50–80° 2θ range (Main diffraction peaks come from $Ti_2AlC_xN_{(1-x)}$. Only clearly visible diffraction peaks from secondary phases are indexed.).

some of the flat denser polished section, only Ti and Al were detected showing the presence of small amounts of titanium aluminides (TiAl and/or $TiAl_2$) in the samples. $Ti_2AlC_xN_{(1-x)}$ compounds were characterized by XRD and Fig. 2a is a typical example of the diffractograms obtained in the 10–80° 2θ range. From these XRD spectra, it appears that the samples are not single phased. In addition to the predominant presence of diffraction peaks from the MAX phase $Ti_2AlC_xN_{(1-x)}$, diffraction peaks attributed to titanium aluminides (TiAl or $TiAl_2$), titanium carbonitrides ($TiC_xN_{(1-x)}$) and Ti_3AlC_2 were observed. Good Rietveld refinements of the XRD data (R_w generally below 10%) allow to quantify the amounts of these secondary phases (this will be more precisely described in the next section). As a general trend, all samples contain very small quantities of titanium aluminides (0–4 wt.%) and titanium carbonitrides (0–2 wt.%), and increasing amounts of Ti_3AlC_2 were obtained for carbon-rich compounds (7.5 and 21.4 wt.% for $x = 0.75$ and $x = 1$, respectively). On the basis of these observations, it is possible to conclude that the large amount of micrograins observed by SEM are $Ti_2AlC_xN_{(1-x)}$ grains. It is important to note that no preferential orientation of these micrograins was evidenced from SEM observations. This is in accordance with the fact that no texture has to be introduced to refine the X-ray diffractograms, and is of importance to the reliability of the amount of the different phases computed from Rietveld refinement. These remarks remain true for all the samples and XRD data discussed in this work.

Fig. 2b shows X-ray diffractograms for different x values in a smaller 2θ range. Two main features are observed: a progressive shift of the diffraction peaks from $Ti_2AlC_xN_{(1-x)}$ towards lower 2θ values when the amount of carbon increases, and a strong broadening of the diffraction peaks for the carbonitrides in comparison to the pure Ti_2AlN and Ti_2AlC.

The first feature is explained by an evolution of the a and/or c lattice parameters of the hexagonal MAX phase. This evolution of the lattice parameters is plotted in Fig. 3. The obtained values are given in Table 1 and compared to literature values. From Rietveld refinements of the XRD data, quite accurate values of the a and c lattice parameters were obtained using the MAUD software. Uncertainties of 5×10^{-5} Å and 5×10^{-4} Å were typically obtained for a and c parameters, respectively. We can immediately note that the a lattice parameter is a linear function of x. Such a linear relation was also observed for the titanium carbonitrides $TiC_xN_{(1-x)}$. A comparison of the evolution of the interatomic distance between Ti atoms in the case of

Table 1
Lattice parameters of $Ti_2AlC_xN_{(1-x)}$ for various carbon contents deduced from Rietveld refinement of XRD spectra (this work). Lattice parameters from the literature are also given. The experimental values from the literature correspond to average values (5 values from Refs.3, 26, 27, 30, 31 for $x = 0$, 2 values from Refs.3,4 for $x = 0.5$ and 22 values from Refs.3,26–29,31,33 for $x = 1$. The associated uncertainty is the standard deviation for $x = 0$ and $x = 1$ and the difference between maximum and minimum values for $x = 0.5$.

	x (C at conc.)					
	0	0.25	0.5	0.75	1	
a (nm)	0.29891(2)	0.30071(1)	0.30250(5)	0.30462(4)	0.30625(5)	This work
	0.29888 ± 0.00018		0.30220 ± 0.0001		0.30515 ± 0.00129	Experimental values from literature
c (nm)	1.3615(1)	1.3605(4)	1.3608(4)	1.3614(5)	1.3668(1)	This work
	1.36123 ± 0.00072		1.36100		1.36423 ± 0.00495	Experimental values from literature

$TiC_xN_{(1-x)}$[25] and $Ti_2Al(C_xN_{(1-x)})$ is also given in Fig. 3(a). These similarities are expected given the close relationships between the $M_{n+1}X_n$ layers of the MAX phase and that of the corresponding binary MX compounds. Even if inhomogeneities in the carbon and nitrogen atomic distribution cannot be excluded, these results evidenced the existence of a random solid solution on the X site. Such a conclusion is in agreement with that of Arròyave and Radovic.[32] On the basis of ab initio investigations, these authors concluded that a short range ordering between C and N atoms is energetically favored, but the C–N interaction is so low that one can easily obtain a random solid solution. The values of the *a* parameter obtained here are in very good agreement with experimental ones from the literature, especially for $x = 0$, 0.5. For $x = 1$, the agreement is good too, but it is worth mentioning that high discrepancies exist for values reported in literature in that case.

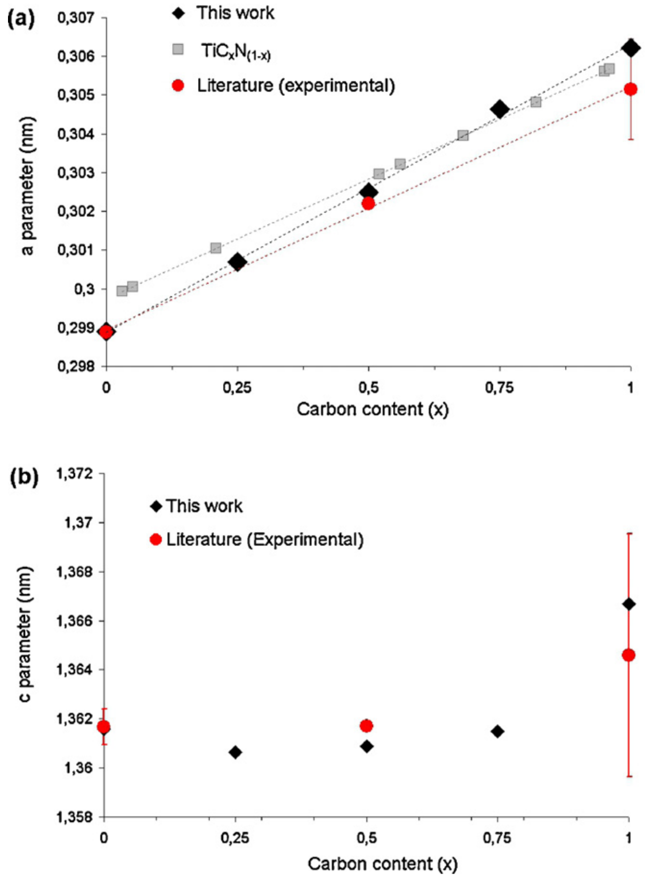

Fig. 3. Evolution of the *a* and *c* lattice parameters ((a) and (b) respectively) as a function of carbon content of the $Ti_2AlC_xN_{(1-x)}$ compound. Values from this work are compared with those reported in literature (average values from several experimental studies), error bars for literature values corresponding to the standard deviation (see Table 1 for further details). In (a), linear regressions are plotted (dashed lines) and the distance *d* between Ti atoms in $TiC_xN_{(1-x)}$ compounds[25] is given for comparison.

In contrast to the case of the *a* parameter, a quite surprising result is obtained for the evolution of the *c* parameter since its value is always lower for carbonitrides than for the pure carbide or pure nitride (but very close to the latter). Such an observation was already reported for $x = 0.5$ by other authors[3,4] and a very similar evolution is obtained for calculated values.[32] This work thus confirms that, at least up to 75% of carbon, carbonitrides have lower *c* values compared to the pure ternary compounds. Further theoretical investigations are required to explain this behavior. Nevertheless, such a decrease in the *c* parameter may reflect a breaking of symmetry of the charge modulation along the *c* axis compared to the one occurring in the defined ternary compounds. Furthermore one will have to explore the range $0.75 \leq x \leq 1$ to determine if this observed decrease of the *c* value is a general trend for the titanium aluminides carbonitrides. On the other hand, one should pay attention on the fact that in the literature, a value of $c = 1.36$ nm is generally reported for Ti_2AlC.[31] By considering this value, one could consider that the value of the *c* parameter remains almost constant irrespective of *x* in $Ti_2AlC_xN_{(1-x)}$. Furthermore, as already mentioned, strong discrepancies exist in the literature for the value of the *c* parameter (see Fig. 3b and Table 1). This is poorly discussed in the literature. Only Pietzka and Schuster[29] noticed this phenomenon and concluded that it can be related to the fact that Ti_2AlC can have a strong carbon deficiency (this will be more discussed in the next section).

The second important feature, the diffraction peak broadening for the carbonitrides (more pronounced for $x = 0.5$), most likely originates from microstrains. Broadening due to a decreasing size of the coherent diffraction domains can be safely excluded since this broadening effect does not occur for some diffraction peaks (especially for $0\,0\,0\,2n$, $n = 1, 2, 3, \ldots$). The fact that the broadening of the diffraction peak varies with the plane index clearly indicates it results from anisotropic microstrains. This is confirmed by the very good quality of Rietveld refinements obtained when considering Popa rules[33]

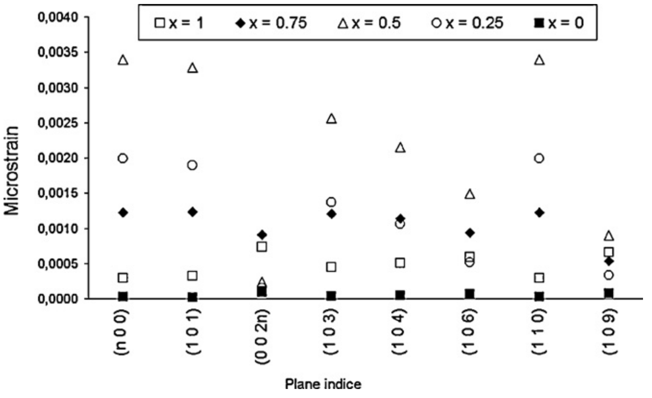

Fig. 4. Microstrain values deduced from Rietveld refinements of the XRD spectra for selected well observable diffractions planes.

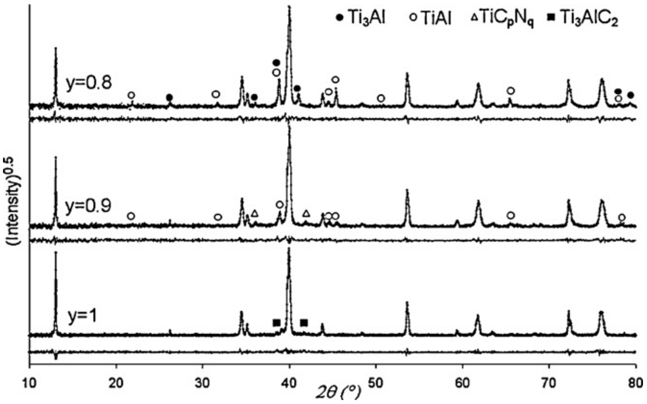

Fig. 5. XRD diffractograms and corresponding Rietveld refinements obtained for $x = 0.25$ for increasing from bottom to top C and N content y in $Ti_2Al(C_xN_{(1-x)})_y$. Residual is plotted below each diffractogram.

for refining the shape of the peaks. As described by Popa, there are relationships between the crystallography of the studied phase and the broadening of the diffraction peaks of different index. In the present case (hexagonal symmetry) three independent microstrain coefficients can be computed to achieve good refinements of all diffraction peaks. Values of the microstrain can thus be determined for all planes; in Fig. 4 are reported these values for the most intense Bragg's reflections. Larger values are obtained for planes perpendicular to the c axis of the hexagonal unit cell. In contrast, almost no microstrain exists along the basal planes (e.g. $(0\,0\,0\,2n)$ planes). This variation in microstrain broadening of the diffraction peaks can be explained by considering carbon and nitrogen concentration gradients. Indeed, small variations in nitrogen and carbon content in the carbonitride lead to different a and c parameter values. In contrast to what happens when using Hot Isostatic Pressure (HIP) methods, slow diffusion processes act during the reactive sintering of the samples and thus larger concentration inhomogeneities on the X site can be obtained for natural sintering. Furthermore, whereas an increase of 10% of carbon in the carbonitride leads to an increase of 0.25% of the a lattice parameter, the related c value is only modified by about 0.02%. In other words, whereas a strongly varies, c remains almost constant for $0 \leq x \leq 0.75$. This fully explains why no noticeable broadening of the $(0\,0\,0\,2n)$ diffraction peaks is observed. In contrast, this will give rise to broad diffraction peaks for nonbasal planes. Finally, it is important to note that this explanation, e.g. the assumption of existing N and C concentration gradients, does not exclude that intrinsic microstrains can exist in MAX phase carbonitrides, but their levels will likely be much lower than those here obtained.

3.2. N and C deficiency in $Ti_2Al(C_xN_{(1-x)})_y$ carbonitrides

In the previous section, we assumed that $y = 1$. One of the main goal of this work is to study the possibility to achieve substoichiometry in carbon and/or nitrogen in $Ti_2Al(C,N)$ compounds and initial amount of the powders were chosen to try to obtain y values varying from 0.7 to 1. For the ideal case, the synthesis of single-phased MAX phase material implies that the desired y value is obtained. If not the case, a multiphased material is obtained and the proportion of $Ti_2Al(C,N)$ is y, it means that no carbon and/or nitrogen substoichiometry is achieved in the MAX phase. For intermediate cases, the true values of x (noted x_t) and y (noted y_t) in the material have to be determined. In the following, x and y designate the stoichiometry of the reactants whereas x_t and y_t as the true values for the product $Ti_2Al(C_{x_t}N_{(1-x_t)})_{y_t}$.

In Fig. 5 are plotted the typical X-ray diffractograms related to decreasing y values. Whatever the value of x is, one observes a contribution of titanium aluminides (TiAl and Ti_3Al) to the XRD spectra that increases with decreasing y values. This increasing amount of these two titanium aluminides is confirmed by SEM and EDX (not shown). Larger dense areas, free of N and C as determined by EDX, can be observed in a backscattering mode whereas the micrograins at the border of these areas and between these last are grains of MAX phase. No noticeable modification of the MAX phase grain size was deduced from SEM observations. From porosimetry experiments, we also note that the samples' density increases when y values decrease. This can simply be explained by the increasing amount of dense intermetallic materials for decreasing values of y.

These observations prove that single-phased material is not obtained in every case and that true values of carbon and nitrogen concentration in the MAX phase has to be determined. Unfortunately, quantification of C and N inside one phase of a multiphased porous material is not obvious since most commonly used techniques determine global C and N concentrations. Therefore we used EELS as a tool to determine C and N concentrations in selected grains of different samples to assess the accuracy of the x_t and y_t values deduced from the phases' quantification obtained from Rietveld refinement of X-ray diffractograms.

All X-ray diffractograms were refined to determine the amount of the different phases in our samples. Fig. 6 gives a summary of the proportion in weight of the different phases present in our samples deduced from these refinements that were all of good quality (R_w values below 10%). As already mentioned, an increasing amount of titanium aluminides (TiAl, Ti_3Al) is observed when $y < 1$. Using fractions of the different phases deduced from these refinements, we computed the true density of the related samples. The values so obtained were very close to those obtained by porosimetry (difference below 1%).

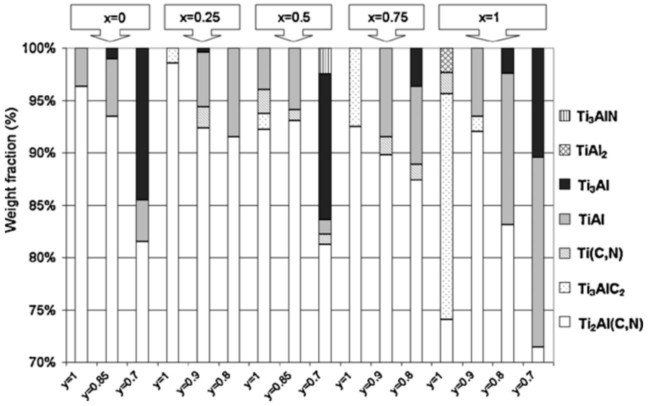

Fig. 6. Weight fractions of the different phases deduced from Rietveld refinements of the X-ray diffractograms for the different values of x and y.

Note that helium picnometry directly gives the true density since we have only open porosity in our samples.

The values of x_t and y_t were then deduced from the following balance equation:

$$2\text{Ti} + \text{Al} + xy\text{C} + (1-x)y\text{N} \rightarrow \alpha_1\text{Ti}_2\text{AlC}_s\text{N}_t + \alpha_2\text{Ti}_3\text{AlC}_2 + \alpha_3\text{TiC}_v\text{N}_w + \alpha_4\text{TiAl} + \alpha_5\text{Ti}_3\text{Al} + \alpha_6\text{TiAl}_2 + \alpha_7\text{Ti}_3\text{AlN} \quad (1)$$

where α_i denotes the molar content of the different products for 1 mole of reactant $\text{Ti}_2\text{Al}(\text{C}_x\text{N}_{(1-x)})_y$. Their values are deduced from weight fractions of the different competeting phases. If we consider the balance for every atomic species, we get:

$$\text{For } T_i: \quad 2 = 2\alpha_1 + 3\alpha_2 + \alpha_3 + \alpha_4 + 3\alpha_5 + \alpha_6 + 3\alpha_7 \quad (2)$$

$$\text{For Al}: \quad 1 = \alpha_1 + \alpha_2 + \alpha_4 + \alpha_5 + 2\alpha_6 + \alpha_7 \quad (3)$$

$$\text{For C}: \quad xy = s\alpha_1 + 2\alpha_2 + v\alpha_3 \quad (4)$$

$$\text{For N}: \quad (1-x)y = t\alpha_1 + w\alpha_3 + \alpha_7 \quad (5)$$

In these relations, s, t, v and w are four unknown parameters one wants to determine. At first, a very simple assumption can be made for v and w (C and N content of the titanium carbonitride): $v \approx x$ and $w \approx (1-x)$. Such an assumption is reasonable because a full solid solution can easily be obtained for titanium carbonitrides and we can consider that C and N concentrations in the formed Ti(C,N) are very similar to those of the reactants. Secondly, and it is the most important consideration, values of α_3 (Ti(C,N) proportion in the products) are very small (the maximum value is 2% and Ti(C,N) presence is noted for only 4 out of 16 studied samples). With such assumptions, s and t can be obtained from:

$$s = \frac{xy(1-\alpha_3) - 2\alpha_2}{\alpha_1} = x_t y_t$$

$$t = \frac{(1-x)y(1-\alpha_3) - \alpha_7}{\alpha_1} = (1-x_t)y_t$$

this leads to:

$$y_t = s + t = \frac{y(1-\alpha_3) - 2\alpha_2 - \alpha_7}{\alpha_1} \quad (6)$$

Table 2
Values of x (carbon content) and y (total stoichiometry in C and/or N) of the reactants compared to the values x_t and y_t of the product $\text{Ti}_2\text{Al}(\text{C}_{x_t}\text{N}_{(1-x_t)}))_{y_t}$ deduced from Rietveld refinements of the XRD diffractograms.

x	x_t	y	y_t
0	0	1	1
0	0	0.85	0.90 ± 0.02
0	0	0.7	0.85 ± 0.02
0.25	0.24 ± 0.01	1	1.00 ± 0.02
0.25	0.25 ± 0.02	0.9	0.92 ± 0.04
0.25	0.25 ± 0.01	0.8	0.86 ± 0.02
0.5	0.49 ± 0.02	1	1.00 ± 0.05
0.5	0.50 ± 0.02	0.85	0.88 ± 0.04
0.5	0.51 ± 0.04	0.7	0.80 ± 0.03
0.75	0.74 ± 0.01	1	0.97 ± 0.03
0.75	0.74 ± 0.02	0.9	0.96 ± 0.04
0.75	0.75 ± 0.02	0.8	0.88 ± 0.04
1	1.00	1	0.89 ± 0.04
1	1.00	0.9	0.95 ± 0.02
1	1.00	0.8	0.96 ± 0.02
1	1.00	0.7	0.98 ± 0.03

$$x_t = \frac{xy(1-\alpha_3) - 2\alpha_2}{y(1-\alpha_3) - 2\alpha_2 - \alpha_7} \quad (7)$$

From this set of equations, x_t and y_t values can thus be easily computed. Nevertheless, this model suffers from uncertainties which have to be considered before analyzing the values of x_t and y_t. The MAUD software we use to perform Rietveld refinement gives uncertainties values for the α_i parameters. These uncertainties strongly vary with the amount of the different phases. Typically, whereas an uncertainty $\Delta\alpha_1 = 0.01$ to 0.02 was obtained for the amount of the main phase ($\text{Ti}_2\text{Al(C,N)}$), relative uncertainties $\Delta\alpha_i/\alpha_i$ varying between 5% and 30% were obtained for the secondary phases, the highest relative uncertainties being obtained for very low values of α_i ($\leq 1\%$). Uncertainties given below for x_t and y_t were computed from uncertainties values given by the software multiplied by a factor 2 to exclude any minimization of the errors. Furthermore, it is important to note that Eqs. (2) and (3) (balance of Ti and Al) were well verified by using α_i parameters obtained from the Rietveld refinement of the XRD data. This constitutes more evidence for considering the values of the α_i parameters used in this work as quite accurate.

Table 2 gives the values of x_t and y_t deduced from (6) and (7) as well as the corresponding uncertainties. Unsurprisingly, the x_t values (true concentration in C of the product) are very close to that of the reactants x. More interesting are the values of nitrogen and/or carbon deficiency we so obtained. In every case, $y_t > y$ (with the noticeable exception $x = 1$; $y = 1$). In other words, single-phased samples are not obtained and the natural reactive sintering process here used does not allow to get a $\text{Ti}_2\text{Al(C,N)}$ material having a large amount of vacancies on the X (N or C) site. Another conclusion that can be addressed from Table 2 is that carbonitrides are able to possess N and C deficiency, the lowest values of y_t being obtained for $x_t = 0.5$. For $\text{Ti}_2\text{AlN}_{y_t}$ (e.g. $x = 0$), nitrogen deficiency can also be obtained but for higher values of y_t. Finally, the case of pure carbides can be considered as quite different. Indeed, whereas no carbon deficiency is obtained

Table 3
Comparison between x_t and y_t values deduced from XRD Rietveld and EELS analysis.

Reactants		Products			
x	y	Rietveld refinement of XRD		EELS	
		x_t	y_t	x_t	y_t
0.5	1	0.49 ± 0.02	1 ± 0.05	0.5 ± 0.05	1 ± 0.1
0.5	0.7	0.51 ± 0.04	0.8 ± 0.03	0.5 ± 0.05	0.76 ± 0.08

for $y < 1$, a lower value of y_t is obtained for $y = 1$. This is a quite surprising result since, in that specific case, C deficiency was not supposed to occur. One can suspect the α_i parameters obtained from Rietveld refinement to be questionable in that case. Another carbide Ti_2AlC sample ($y = 1$) was synthesized and very similar amounts of the different phases were obtained. Furthermore the fact that Ti_2AlC and Ti_3AlC_2 are the only carbide phases identified on the X-ray spectra reveals that carbon deficiency in Ti_2AlC and/or in Ti_3AlC_2 compounds has to be considered to fully explain the carbon balance. For $y < 1$, no or almost no carbon understoichiometry is obtained for Ti_2AlC and this allows to propose that Ti_3AlC_2 can be carbon deficient whereas it is not the case for Ti_2AlC. For $x = y = 1$, assuming that carbon deficiency can only occur for $Ti_3AlC_{(2-x)}$, new balance equations give a stoichiometry $Ti_3AlC_{1.5}$ for the 312 MAX phase. This conclusion (e.g. almost no carbon deficiency can be achieved in Ti_2AlC compound) is in contradiction with results reported by Pietzka and Schuster[23] who concluded that a value of $y_t = 0.7$ is generally obtained for $Ti_2AlC_{y_t}$. It is quite difficult to understand this difference since our study unambiguously shows that, after 4 h at 1400 °C, we do not obtain carbon understoichiometry in this compound, even when the reactants where chosen so that $y = 0.7$. In their work, Pietzka and Schuster used the same reactants (e.g. Ti, Al and C powders) but with longer annealing time (20 h at 1375 °C or 15 h at 1485 °C in[23] or 20 h at 1300 °C in29). It is possible that thermodynamic equilibrium was reached in Pietzka's studies whereas it is not the case for the present one (4 h at 1400 °C in an open system). The C and N carbon concentration gradient outlined in the previous section can also be explained by the short annealing time. The products obtained in this study should then be considered as representatives of those generally obtained after a conventional heat treatment rather than those obtained at thermodynamic equilibrium at 1400 °C.

To assess the main conclusions of this work addressed on the basis of Rietveld refinement of X-ray diffractograms, two samples ($x = 0.5$ and $y = 1$; $x = 0.5$ and $y = 0.8$) were examined in a TEM. The C and N contents of these two samples were also deduced from EELS investigations for comparison. The nanolamellar structure of the MAX phase was easily evidenced in high resolution images of some grains (not shown) and EELS spectra were recorded on areas presenting electron diffraction patterns characteristic of the MAX phase. The C and N content of the two MAX phase carbonitrides obtained from EELS are given in Table 3. Like it was found from Rietveld analysis of the XRD data, values of x_t are very close to that of x. The excellent agreement between values deduced from EELS experiments and Rietveld refinement of XRD confirms that C and N deficiency can be obtained for $Ti_2AlC_xN_{(1-x)}$ compounds. Finally, it is important to mention that no O–K edge was observed on the EELS spectra, e.g. the two probed samples do not contain any noticeable amount of oxygen (O–K edge is observable even for small amounts of oxygen). This is an important result since it rules out the possibility of oxygen incorporation on the X site for N and C deficient carbonitride samples as it is the case for $Ti_2Al(C,O)$ compounds.

On the basis of XRD results, it is also possible to extract the evolution of the a and c lattice parameters for the various values of x_t and y_t of the $Ti_2Al(C_xN_{(1-x)})_y$ compounds. The evolution of the lattice parameters is plotted in Fig. 6. Whereas a very slight decrease of the a parameter is observed when y_t decreases, it is the reverse concerning the c parameter. For pure carbides ($x = 1$), the values of a and c parameters are not reported for $y = 1$ since the y_t value is questionable in that case. Again, for same values of y_t, c values for the carbonitrides are lower than pure nitride and carbide ones. On the opposite, a values seem to obey to a Vegard's law irrespective of y_t, as well as cell volumes. We can also note that the unit cell volumes remain almost constant whatever y_t is for a given x_t (Fig. 7c). Very similar values can be deduced from values reported in literature excepted for Pietzka and Schuster[23] ones that are slightly different.

One note only very slight modifications of the unit cell parameters when C and N deficiencies are taken into account. Nevertheless, this last figure clearly shows, with the exception of the pure carbide Ti_2AlC, that small discrepancies will be found for unit cell parameters of some MAX phases if assuming exact 211, 312 or 413 stoichiometries as it is generally considered in the literature dedicated to the determination of the unit cell parameters of MAX phases, either from ab initio calculations or from experiments. Again, the carbide case has to be outlined. On the basis of the obtained values of the carbon stoichiometry for this compound, the present study indicates that Ti_2AlC can be considered as a definite compound with carbon content close to one. On the other hand, the a and c lattice parameters slightly vary (see Fig. 7b and c for $x = 1$) and, as already noticed in the previous section, strong discrepancies exist in the literature as far as these lattice parameters are concerned. Such observations will tend to prove, on the contrary, that Ti_2AlC is not a definite compound as already mentioned by Pietzka and Schuster[23] Such a contradiction asks of course for more detailed studies. One can propose that other considerations should be taken into account to better explain these discrepancies. For instance, some studies show that many stacking faults can exist in Ti_2AlC.[34] In such a case, values of the lattice parameters conventionally deduced from X-ray diffractograms can be strongly different from that of

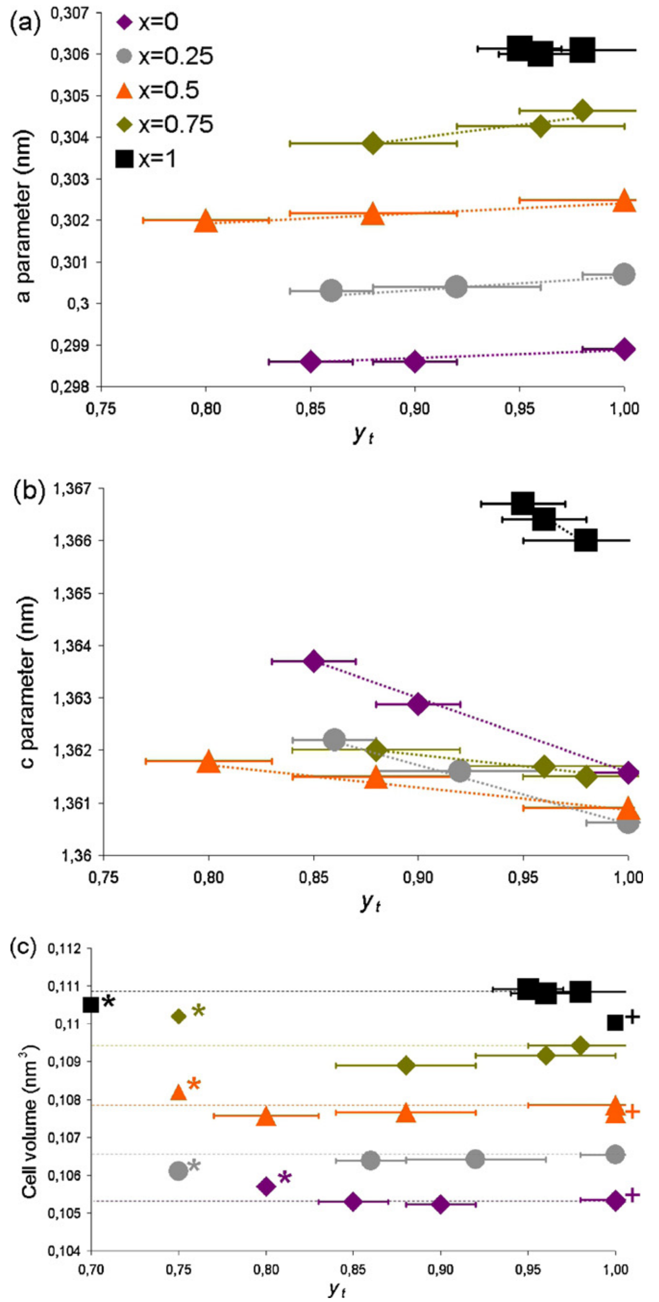

Fig. 7. Evolution of the *a* (a), *c* (b) lattice parameters and (c) unit cell volume of the $Ti_2Al(C_{x_t}N_{(1-x_t)}))_{y_t}$ compounds with respect to x_t and y_t. In (c), values having a star or a cross at their right come from[23] or correspond to average values from the literature (see Table 1), respectively. Only error bars for y_t are indicated (corresponding to values given in Table 2), error bars for lattice parameters being too small to be clearly observable (typically 5×10^{-5} nm, 5×10^{-4} nm and 7×10^{-4} nm^3 for *a*, *c* lattice parameters and unit cell volume, respectively, in the case of this study).

a fault-free phase. Finally, it must be outlined that in the present study, the lattice parameters of the compounds with nitrogen and carbon deficiencies remain almost constant irrespective of y_t, whereas it is not the case for Ti_2AlC which has no or little carbon deficiency. Such an observation being opposite to what is generally observed for defined compounds, it appears that more detailed theoretical and experimental works are needed to better understand this phenomenon in $Ti_2Al(C_xN_{(1-x)})_y$.

4. Conclusions

$Ti_2Al(C_xN_{(1-x)})_y$ MAX phases carbonitrides were synthesized by reactive natural sintering for 4 h at 1400 °C. As a main result, carbon- and/or nitrogen-deficiency can be achieved for the carbonitrides and nitrides but not for the carbides. The highest degree of carbon and nitrogen substoichiometry can be obtained for the carbonitrides, especially for $y = 0.5$. Irrespective of the amount of the carbon and nitrogen vacancies, the *a* unit cell parameter obeys a Vegard's law whereas the *c* lattice parameter of the carbonitrides is smaller than that of the end members. At this moment, it is not possible to fully explain why it is possible to achieve to obtain higher degree of substoichiometry (e.g. lower value of *y*) in solid solutions than in the pure carbide and nitride and why the *c* unit cell parameter value of the carbonitrides is lowered. There is therefore a need for theoretical studies on these specific points.

Only slight evolutions of the *a* and *c* lattice parameters are observed by varying *y*. Nevertheless, it can explain the small discrepancies observed about the unit cell parameters values reported in the literature for MAX phases, especially for those which are not defined compounds. Indeed, this study shows that quite important deviations from the "ideal" stoichiometry of the MAX phases can be achieved. Precise values of the stoichiometry of the MAX phase compounds need thus to be considered when the structure (e.g. unit cell parameters) or the properties are described.

Acknowledgement

The University of Poitiers is acknowledged for funding a Visiting Professor position for P.E.

References

1. Eklund P, Beckers M, Jansson U, Högberg H, Hultman H. The $M_{n+1}AX_n$ phases: materials science and thin-film processing. *Thin Solid Films* 2010;**518**:1851–78.
2. Wang JY, Zhou YC. Recent progress in theoretical prediction, preparation, and characterization of layered ternary transition-metal carbides. *Annu Rev Mater Res* 2009;**39**:10.1–29.
3. Barsoum MW, Ali M, El-Raghy T. Processing and characterization of Ti_2AlC, Ti_2AlN and $Ti_2AlC_{0.5}N_{0.5}$. *Metall Mater Trans A* 2000;**31**:1857–65.
4. Radovic M, Ganguly A, Barsoum MW. Elastic properties and phonon conductivities of $Ti_3Al(C_{0.5}N_{0.5})_2$ and $Ti_2Al(C_{0.5}N_{0.5})$ solid solutions. *J Mater Res* 2008;**23**:1517–21.
5. Du YL, Sun ZM, Hashimoto H, Barsoum MW. Theoretical investigations on the elastic and thermodynamic properties of $Ti_2AlC_{0.5}N_{0.5}$ solid solution. *Phys Lett A* 2009;**374**:78–82.
6. Wilhelmsson O, Palmquist JP, Lewin E, Emmerlich J, Eklund P, Persson POÅ, et al. Deposition and characterization of ternary thin films within the Ti–Al–C system by DC magnetron sputtering. *J Cryst Growth* 2006;**291**:290–300.
7. Persson POÅ, Rosén J, McKenzie DR, Bilek MMM, Höglund C. A solid phase reaction between TiC_x thin films and Al_2O_3 substrates. *J Appl Phys* 2008;**103**:066102.

8. Persson POÅ, Rosén J, McKenzie DR, Bilek MMM. Formation of the MAX-phase oxycarbide $Ti_2AlC_{1-x}O_x$ studied via electron energy-loss spectroscopy and first-principles calculations. *Phys Rev B* 2009;**80**:092102.
9. Persson POÅ, Höglund C, Birch J, Hultman L. $Ti_2Al(O,N)$ formation by solid-state reaction between substoichiometric TiN thin films and Al_2O_3 (0 0 0 1) substrates. *Thin Solid Films* 2011;**519**:2421–5.
10. Dahlqvist M, Alling B, Abrikosov IA, Rosén J. Stability trends of *MAX* phases from first principles. *Phys Rev B* 2010;**81**:024111.
11. Pierson HO. In: Westwood N, editor. *Handbook of refractory carbides and nitrides*. Noves Publications; 1996.
12. Williams WS. Electrical properties of hard metals. *Int J Refract Met Hard Mater* 1999;**17**:21–6.
13. Williams WS. The thermal conductivity of metallic ceramics. *J Miner* 1998;**50**:62–6.
14. Dolique V, Jaouen M, Cabioc'h T, Pailloux F, Guérin Ph Pélosin V. Formation of (Ti,Al)N/Ti_2AlN multilayers after annealing of TiN/TiAl(N) multilayers deposited by ion beam sputtering. *J Appl Phys* 2008;**103**:083527.
15. Rawn CJ, Barsoum MW, El-Raghy T, Procopio A, Hoffmann CM, Hubbard CR. Structure of Ti_4AlN_3 – a layered $M_{n+1}AX_n$ nitride. *Mater Res Bull* 2000;**35**:1785–96.
16. Tzenov N, Barsoum MW. Synthesis and characterization of $Ti_3AlC_{1.8}$. *J Am Ceram Soc* 2000;**83**:825–32.
17. Etzkorn J, Ade M, Hillebrecht H. V_2AlC, V_4AlC_{3-x} ($x \approx 0.31$) and $V_{12}Al_3C_8$ – synthesis, crystal growth, structure, and superstructure. *Inorg Chem* 2007;**46**:7646–53.
18. Music D, Ahjua R, Schneider JM. Theoretical study of nitrogen vacancies in Ti_4AlN_3. *Appl Phys Lett* 2005;**86**:031911.
19. Dahlqvist M, Alling B, Rosén J. Stability trends of MAX phases from first principles. *Phys Rev B* 2010;**81**:220102.
20. Du YL, Sun ZM, Hashimoto H, Tian WB. First-principles study of carbon vacancy in Ta_4AlC_3. *Mater Trans* 2008;**49**:1934–6.
21. Eklund P, Palmquist JP, Höwing J, Trinh DH, El-Raghy T, Högberg H, et al. Ta_4AlC_3: phase determination, polymorphism and deformation. *Acta Mater* 2007;**55**:4723–9.
22. Etzkorn J, Ade M, Hillebrecht H. Ta_3AlC_2 and Ta_4AlC_3 – single crystal investigations of two new ternary carbides of tantalum synthesized by the molten metal technique. *Inorg Chem* 2007;**46**:1410–8.
23. Pietzka MA, Schuster JC. Phase equilibria in the quaternary system Ti–A1–C–N. *J Am Ceram Soc* 1996;**79**:232l–330l.
24. Lutterotti L. *Materials Analysis Using Diffraction (MAUD) software*, http://www.ing.unitn.it/~maud/.
25. Wokulska K. Thermal expansion of whiskers of Ti(C,N) solid solution. *J Alloy Compd* 1998;**264**:223–7.
26. Manoun B, Zhang FX, Saxena SK, El-Raghy T, Barsoum MW. X-ray pressure study of Ti_2AlN and Ti_2AlC. *J Phys Chem Solids* 2006;**67**: 2091–4.
27. Hug G, Jaouen M, Barsoum MW. X-ray absorption spectroscopy, EELS, and full-potential augmented plane wave study of the electronic structure of Ti_2AlC, Ti_2AlN, Nb_2AlC, and $(Ti_{0.5}Nb_{0.5})_2AlC$. *Phys Rev B* 2005;**71**:024105.
28. Schuster J, Nowotny H, Vaccaro C. The ternary systems: Cr–Al–C, V–Al–C, and Ti–Al–C and the behavior of H-phases (M_2AlC). *J Solid State Chem* 1980;**32**:213–9.
29. Pietzka MA, Schuster JC. Summary of constitutional data on the aluminium-carbon-titanium system. *J Phase Equilib* 1994;**15**:392–400.
30. Gamamik MY, Barsoum MW, El-Raghy T. Improved X-ray powder diffraction data for Ti_2AlN. *Powder Diffraction* 2000;**15**:241–2.
31. Nowotny H. Struktuchemie Einger verbindungen der ubergangsmetalle mit den elementen C, Si, Ge, Sn. *Prog Solid State Chem* 1970;**2**:27–70.
32. Arróyave R, Radovic M. Ab initio investigation of $Ti_2Al(C,N)$ solid solutions. *Phys Rev B* 2011;**84**:134112.
33. Popa C. The ($h\,k\,l$) dependence of diffraction-line broadening caused by strain and size for all Laue groups in Rietveld refinement. *J Appl Crystallogr* 1998;**31**:176–80.
34. Lin ZJ, Zhuo MJ, Zhou YC, Li MS, Wang JY. Microstructural characterization of layered ternary Ti_2AlC. *Acta Mater* 2006;**54**:1009–15.