

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

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## 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  $0.7 \leq y \leq 1$ . 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.

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## 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.<sup>1</sup> 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<sup>3-5</sup> 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,<sup>6</sup> or due to a reaction between a TiC, TiN, or  $Ti_2AlC$  film with an  $Al_2O_3$  substrate.<sup>7-9</sup> 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%.<sup>10</sup>

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  $TiC_{0.98}$ <sup>11</sup> and some of its physical properties (e.g. electrical resistivity, thermal

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conductivity)<sup>12,13</sup> 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<sub>2</sub>AlN,<sup>14</sup> Ti<sub>4</sub>AlN<sub>3</sub>,<sup>15</sup> Ti<sub>3</sub>AlC<sub>2</sub>,<sup>16</sup> and V<sub>4</sub>AlC<sub>3</sub>,<sup>17</sup> 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<sub>4</sub>AlN<sub>3- $\delta$</sub>  and V<sub>4</sub>AlC<sub>3- $\delta$</sub> , respectively, increases the phase stability relative to the stoichiometric 413 phases.<sup>18,19</sup> In contrast, a similar calculation for  $\alpha$ -Ta<sub>4</sub>AlC<sub>3</sub> suggests that a small amount of C vacancies in Ta<sub>4</sub>AlC<sub>3</sub> reduces its stability compared to the stoichiometric structure,<sup>20</sup> and there are no experimental indications that  $\alpha$ -Ta<sub>4</sub>AlC<sub>3</sub> is understoichiometric in C.<sup>21,22</sup> 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<sup>23</sup> reported a continuous range of solid solutions in Ti<sub>2</sub>Al(C<sub>x</sub>N<sub>1-x</sub>)<sub>0.8</sub>, 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<sub>2</sub>Al(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<sub>2</sub>Al(C<sub>x</sub>N<sub>1-x</sub>)<sub>y</sub> 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)yN. 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<sup>TM</sup> 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<sup>TM</sup>) 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 pycnometry. 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 K $\alpha$  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 2 $\theta$  range (10–80°) covers most of the intense peaks of Ti<sub>2</sub>AlC<sub>x</sub>N<sub>1-x</sub>. The instrument was operating at 40 kV and 40 mA. Steps interval of 0.02° or 0.03° (2 $\theta$ ) and counting time varying between 5 and 20 s for each step were used. The pattern of a Cr<sub>2</sub>O<sub>3</sub> 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.<sup>24</sup>

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<sub>2</sub>AlC<sub>x</sub>N<sub>(1-x)</sub> carbonitrides

Results obtained on Ti<sub>2</sub>AlC<sub>x</sub>N<sub>(1-x)</sub> 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  $\mu$ m 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 K $\alpha$  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

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