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Synthesis and characterization of a new $(\text{Ti}_{1-y}\text{Cu}_y)_2(\text{Al}_{1-x}\text{Cu}_x)\text{C}$ MAX phase solid solution

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ABSTRACT

New $[\text{Ti}_{(1-y)}\text{Cu}_y]_2[\text{Al}_{(1-x)}\text{Cu}_x]\text{C}$ solid solutions have been synthesized by solid-state reaction performed at 760 and 800 °C on compacted Ti_2AlC -40 vol % Cu composite particles produced by mechanical milling. Using XRD and EDXS, it is demonstrated that Cu atoms can enter the crystallographic structure of the Ti_2AlC MAX phase, whereas a $\text{Cu}(\text{Al})$ solid solution is formed during thermal treatment. A selective chemical etching of the $\text{Cu}(\text{Al})$ matrix is performed to determine the composition of the MAX phase solid solution by analyzing the filtrate and the solid phase using ICP-OES and EDXS methods respectively. $(\text{Ti}_{0.85}\text{Cu}_{0.15})_2(\text{Al}_{0.75}\text{Cu}_{0.25})\text{C}$ and $(\text{Ti}_{0.85}\text{Cu}_{0.15})_2(\text{Al}_{0.58}\text{Cu}_{0.42})\text{C}$ solid solutions are formed after thermal treatment at 760 and 800 °C, respectively. The substitution rate on the A site of the MAX phase thus increases with temperature.

1. Introduction

$\text{M}_{n+1}\text{AX}_n$ phases (with $n = 1-3$) form a wide class of nanolaminated ternary carbides or nitrides, with a hexagonal structure; M stands for an early transition metal, A for an A-group element (from IIIA to VIA) and X for either carbon or nitrogen [1–10]. MAX phases crystallize in the hexagonal space group $P63/mmc$. They consist of M_{n+1}X_n layers (characterized by strong covalent M-X bonds) interleaved with A layers (weaker M-A bonds). This inherent nanolayered structure provides a unique combination of metal-like and ceramic-like properties: machinability, good electrical and thermal conductivity, high thermal shock resistance, good oxidation resistance, stiffness at high temperature [9] which opens a way to diverse potential applications. In addition to the considerable possibilities of changing the chemistry of these systems by playing on the M, A or X elements, solid solutions can also be synthesized on every one of these three atomic sites, thereby allowing the tuning of their electronic, mechanical, optical or thermal properties [11–18]. Moreover, because of the combination of their nanolaminated structure and versatile chemistry, these materials are precursors for a new class of two-dimensional materials, the MXenes [19–22]. Indeed, Naguib et al. demonstrate that MAX phases can be considered as precursor materials to produce two-dimensional carbides by simple exfoliation of the A atom layers [23,24]. It has also been shown that

nanocomposite materials can be formed by intimate reaction between a metallic element and the A layers [25]. In such a context, the wetting behavior of an Ag–Cu eutectic melt on the deoxidized surface of Ti_3SiC_2 has been shown to be very similar to a metal-to-metal wetting [26] and Dezellus et al. have demonstrated that Cu atoms can enter the crystallographic structure of the Ti_3SiC_2 MAX phase [27]. Nechiche et al. heat-treated Ti_3AlC_2 -40 vol.% Cu composite particles at 760 °C to synthesize a new $(\text{Ti}_{1-x}\text{Cu}_x)_3(\text{Al}_{1-x}\text{Cu}_x)\text{C}_2$ MAX phase solid solution [28,29]. Cu atoms enter the crystal structure of Ti_3AlC_2 , and it is mainly located at the A site of MAX phase. The substitution rate of Al by Cu is in the range 48–51 %, while the substitution rate of Ti by Cu is in the range 3–7 %. Li et al. [30] also synthesized $\text{Ti}_3(\text{Al}_{1-x}\text{Cu}_x)\text{C}_2$ phase with a degree of ordering in the A plane via the A site replacement reaction in CuCl_2 molten salt. Ding et al. [31] synthesized new $\text{Ti}_2(\text{Al}_{1-x}\text{Cu}_x)\text{N}$ and Nb_2CuC MAX phases by A-site replacement by reacting Ti_2AlN and Nb_2AlC , respectively, with CuCl_2 or CuI molten salt. Complete A-site replacement in Nb_2AlC leads to the formation of Nb_2CuC . However, the replacement of Al in Ti_2AlN phase was only close to complete with a $\text{Ti}_2(\text{Al}_{0.1}\text{Cu}_{0.9})\text{N}$ composition. Similarly, the substitution reaction between the Zn element in molten ZnCl_2 salt and the Al element in the following MAX phases - Ti_3AlC_2 , Ti_2AlC , Ti_2AlN and V_2AlC - can be used to occupy the A site in the pre-existing MAX phase structure to synthesize new MAX phases [32,33].

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As solid solution effects are able to induce magnetism [34,35], to tune some physical properties such as transport properties [17,36] and to stabilize MXene carbides, nitrides, carbonitrides [37–40] or recent MAX phases compounds (such as $(\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n$ with $n = 1, 2$ and 3) [41], the existence of $\text{M}_x\text{Cu}_y\text{A}_z\text{X}_2$ MAX phases is of major importance. Indeed, Cu-containing MAX phases likely induce a modification of the electronic properties of the materials, compared with the reference system, and may play a key role in the high-power microelectronic devices realized on SiC substrates [42–46]. The synthesis of $\text{M}_x\text{Cu}_y\text{A}_z\text{X}_2$ MAX phases can also allow producing new MXenes containing Cu atoms which may offer new opportunities for potential applications of MXenes.

The goal of this study consists in expanding the family of MAX phase solid solution and more specifically in demonstrating that alloying Ti_2AlC with Cu (transition metal with a full d band) is possible using a powder metallurgy route.

2. Experimental details

Home-made Ti_2AlC and commercial Cu (3–5 μm , 99.9 % purity) powders were selected as starting materials. The Ti_2AlC MAX phase used in this work was synthesized by thermal treatment of a $\text{Ti}:0.9\text{T}:1.1\text{Al}$ powder mixture using the procedure described in Ref. [47]. The as-synthesized bulk Ti_2AlC was crushed into powder in order to obtain particles whose sizes are in the range 80–200 μm . To prepare homogeneous Ti_2AlC -40 vol% Cu mixtures, Ti_2AlC and Cu powders were homogenized in a Turbula® mixer. The resulting powder mixture was mechanically ball-milled for 20 min in enclosed air with a vibratory ball mill (SPEX 8000) using stainless-steel container and balls, and a ball-to-powder mass ratio of 5:1. Thus, a green sample was produced by cold-compaction using a uniaxial pressure of 300 MPa. The green compact was embedded in a glass container under vacuum and heat treated in the 760–800 °C temperature range during 2 h under argon atmosphere; the heating and cooling rates were fixed at 10 °C/min.

After thermal treatment, samples were grinded using SiC papers and then polished with a diamond suspension. Finally, a chemo-mechanical polishing was performed using a neutral suspension of alumina nanoparticles. Such a polishing allows producing a very flat surface and it avoids any work hardening due to conventional grinding.

The microstructure of the Ti_2AlC and Cu co-milled powders as well as the microstructure of the heat-treated end-product were examined using a high resolution, Field-Emission Scanning Electron Microscope (FESEM

Jeol 7001F-TTLs) coupled with Energy-Dispersive X-ray Spectrometry (EDXS, Oxford Instruments) for chemical analyses.

Phase identification was performed by X-Ray Diffraction (XRD) using a Bruker D8 diffractometer with Cu-K α 1 radiation. XRD data were refined using the Materials Analysis Using Diffraction (MAUD) [48] software to extract the lattice parameters and the volume content of the different phases.

A selective chemical etching was performed with nitric acid (68 wt %) during 20 min on the heat-treated end-product in order to dissolve metallic phases (potentially Ti, Cu and Al metals). After filtration on a sintered glass, the chemical composition of the filtrate was analyzed using Inductively Coupled Plasma-Optic Emission Spectrometer (ICP-OES, PerkinElmer Optima 2000 DV) whereas the solid phase was weighted and further characterized by XRD and FESEM.

3. Results and discussion

Fig. 1a shows the X-ray diffraction pattern of the Ti_2AlC powders resulting from thermal treatment at 1450 °C for 3 h starting with a 0.9TiC + Ti + 1.1Al powder mixture. For comparison, the XRD pattern of the Ti_2AlC -40 vol% Cu composite particles obtained after mechanical milling in the vibratory ball-mill is reported in Fig. 1b. In order to avoid mechanical alloying of Ti_2AlC and Cu powders during milling operation, the milling time was short and limited to 20 min. Indeed, as shown in Fig. 1b, no peaks other than those of the Ti_2AlC and Cu starting reactants are observed in the XRD pattern of these vibratory milled blends. Moreover, one can note that XRD peaks of the milled composite particles broaden due to the decrease of X-ray coherent domain size and likely due to the presence of microstrains.

A representative back-scattered SEM micrograph of the cross-section of a composite particle produced by high energy ball milling and embedded in a conductive resin, is shown in Fig. 2a. Ball-milling of Ti_2AlC and Cu powders leads to the formation of aggregates composed of alternative layers of MAX (dark contrast) and Cu (bright contrast) phases, as confirmed using EDXS analyses. As observed in Fig. 2b, the composite particles have an intimate sandwich-type microstructure characteristic of the fracture, deformation and welding events occurring during mechanical milling [49,50].

XRD patterns of the heat-treated end-products at 760 °C and 800 °C are shown in Fig. 3. Ti_2AlC and Cu phases detected after ball-milling are still present after heat treatment, whereas one can also distinguish X-ray

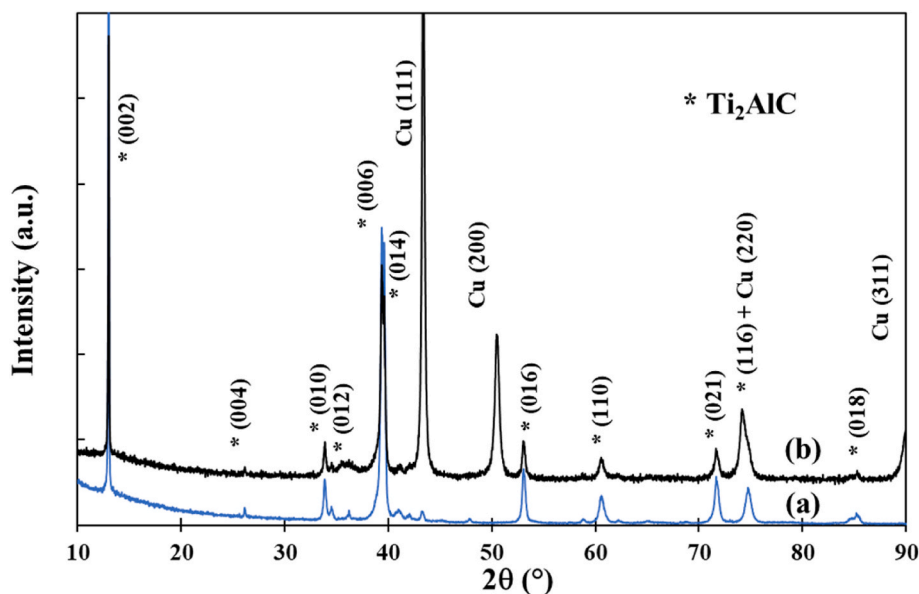


Fig. 1. X-ray diffraction patterns of (a) Ti_2AlC powders obtained after thermal treatment performed (a) at 1450 °C for 3 h and (b) Ti_2AlC -40 vol% Cu composite particles obtained after mechanical milling in the vibratory ball-mill ($R_{\text{bp}} = 5:1$, 20 min).

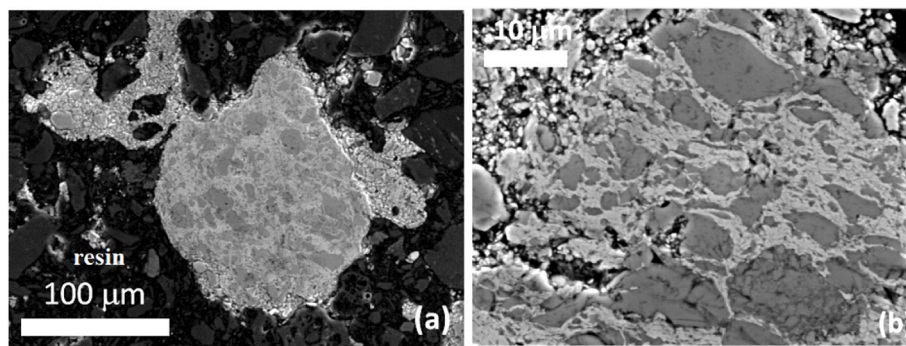


Fig. 2. Back-scattered FESEM micrographs of the cross-section of a Ti_2AlC -Cu composite particle produced by mechanical milling, (a) general view, (b) closer view of the sandwich type microstructure.

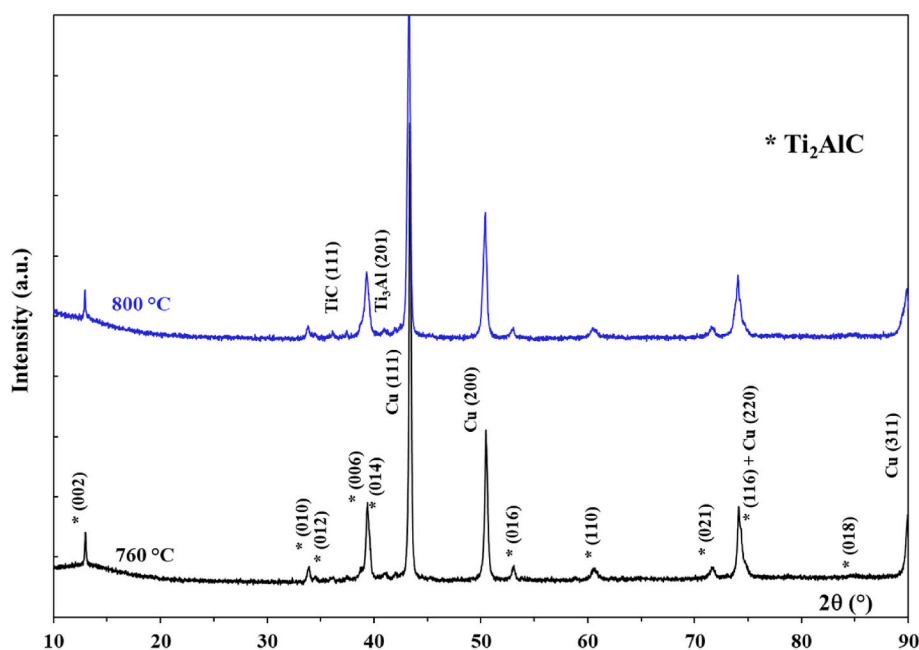
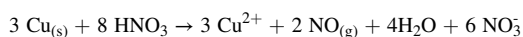


Fig. 3. X-ray diffraction patterns of the Ti_2AlC -40 vol% Cu composite particles obtained after mechanical milling in the vibratory ball-mill ($R_{bp} = 5:1$, 20 min) and heat treated at 760 °C (black line) and 800 °C (blue line).

diffraction peaks of TiC and Ti_3Al . After thermal treatment, we can also note the intensity decrease of the (002) and (004) Ti_2AlC peaks, and the slight shift of the Cu peaks towards lower angles. The shift of the Cu peaks towards higher lattice parameters may suggest the formation of a solid solution of Al into Cu resulting from the diffusion and subsequent partial dissolution of Al atoms constituting the MAX phase into Cu during thermal treatment. Indeed, after ball-milling, the intimate microstructure promotes large contact areas between Ti_2AlC and Cu reactants which decrease diffusion path lengths and increase reactivity during the subsequent thermal treatment. Furthermore, the intensity variation of the (00l) diffraction peaks of the MAX phase can be due to a modification of the Ti_2AlC structure by adding Cu in the crystal network.

Using Rietveld method, the refinement of the XRD pattern shows that the substitution of Cu atoms in Al positions of MAX crystal leads to a drastic decrease of the (00l) peaks intensities of Ti_2AlC and a disappearance of the Ti_3AlC_2 (00l) peaks [29]. In fact, the presence of Cu in Al sites decreases diffusion factors corresponding to (00l) Ti_2AlC family planes.

A selective chemical etching with nitric acid during 20 mn has been performed in order to dissolve the copper matrix:



After filtration on a sintered glass, one can obtain the solid solution and the filtrate containing metallic ions.

The XRD patterns of the solid phases obtained after chemical etching and subsequent filtration of the $\text{Ti}_2\text{AlC}/\text{Cu}$ composites treated at 760 and 800 °C are shown in Fig. 4. By comparing Figs. 1, 3 and 4, one can observe that Cu diffraction peaks related to the Cu(Al) solid solution have disappeared after chemical etching. Consequently, one can conclude that the solid phase obtained after chemical etching and subsequent filtration is mainly composed of the $(\text{Ti}_{1-y}\text{Cu}_y)_2(\text{Al}_{1-x}\text{Cu}_x)\text{C}$ solid solution. A more detailed analysis of the XRD pattern allows demonstrating that TiC, TiAl and Ti_3Al are formed at 760 °C and 800 °C whereas some Ti_3AlC_2 and Ti_2Al_5 are also detected after thermal treatment at 800 °C. Table 1 gives the weight percentages of the different secondary phases (impurities) formed at 760 and 800 °C, whereas Table 2 gives the cell parameters of the different major solid phases, as determined from Rietveld refinement analysis.

Back-scattered SEM observations and corresponding EDXS analyses have been performed on several grains of the $\text{Ti}_2\text{AlC}/\text{Cu}$ composite samples heat-treated at 760 °C and 800 °C and chemically etched with nitric acid. Fig. 5 shows the corresponding micrographs whereas EDXS results, obtained with an electron beam energy of 5 keV in order to minimize the interaction volume of the electron beam, are reported in

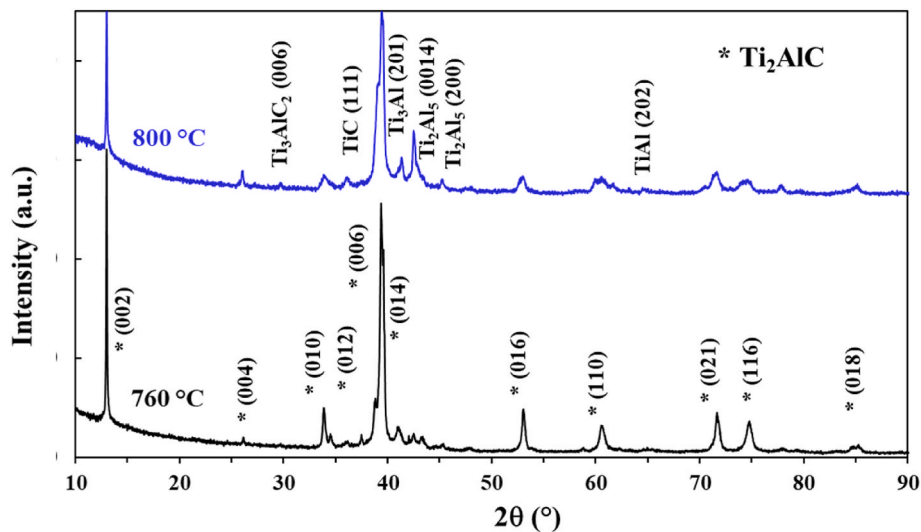


Fig. 4. X-ray diffraction patterns of the Ti_2AlC -40 vol% Cu composite particles obtained after mechanical milling in the vibratory ball-mill ($R_{bp} = 5:1$, 20 min), heat treated at 760 °C (black line) and 800 °C (blue line) and chemically etched.

Table 1

Quantity of the different impurities determined via Rietveld refinement after chemical etching and subsequent filtration of the Ti_2AlC /Cu composites heat treated at 760 and 800 °C.

Rietveld refinement	TiAl (wt.%)	TiC (wt.%)	Ti_3Al (wt.%)	Ti_3AlC_2 (wt.%)	Ti_2Al_5 (wt.%)
MAX phase solid solution obtained at 760 °C	7,0±0,7	3,5 ± 0,4	2,0±0,2	0	0
MAX phase solid solution obtained at 800 °C	2,0±0,2	6,0 ± 0,6	3,0 ± 0,3	3,0±0,3	6,0±0,6

Table 3. After thermal treatment at 760 °C, a single contrast is observed in Fig. 5a although multiphase areas have also been observed, consistently with Rietveld analyses. However, after thermal treatment at 800 °C, it can be noted, in Fig. 5b, that at least 3 contrasts are observed

Table 2

Cell parameters of the different major solid phases determined via Rietveld refinement after chemical etching and subsequent filtration of the Ti_2AlC /Cu composites heat treated at 760 and 800 °C.

	Ti_2AlC	Solid solution obtained at 760 °C	Solid solution obtained at 800 °C
a (Å)	3.0592 ± 0.0004	3.0598 ± 0.0004	3.070 ± 0.001
c (Å)	13.658 ± 0.002	13.673 ± 0.002	13.743 ± 0.006

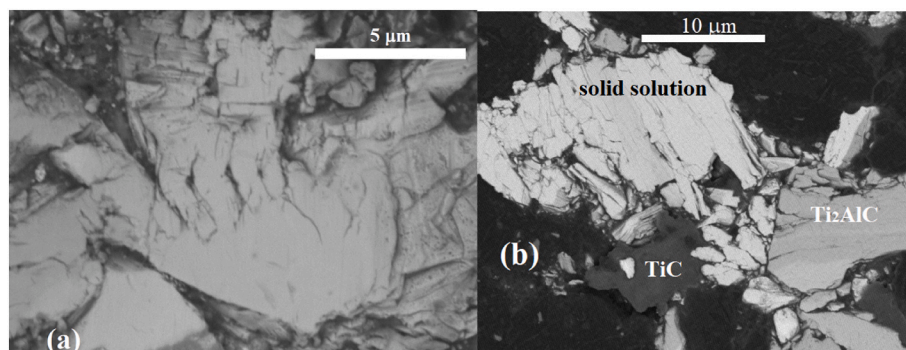


Fig. 5. FESEM back-scattered view of the MAX phase solid solution heat treated at 760 °C (a) and 800 °C (b), chemically etched and filtrated.

Table 3

Average chemical compositions of the two solid solutions determined from EDXS analyses and calculated from deduced compositions of the solid phases by ICP-OES.

Measured by EDXS analyses	Ti (at. %)	Al (at. %)	C (at. %)	Cu (at. %)
MAX phase solid solution obtained at 760 °C	45 ± 2	19 ± 2	22 ± 4	14 ± 2
MAX phase solid solution obtained at 800 °C	44 ± 1	16 ± 2	22 ± 4	18 ± 2
Calculated from deduced composition of the solid solution by ICP-OES	Ti (at. %)	Al (at. %)	C (at. %)	Cu (at. %)
MAX phase solid solution obtained at 760 °C	42 ± 1	19 ± 1	25	14 ± 1
MAX phase solid solution obtained at 800 °C	43 ± 1	14 ± 2	25	18 ± 2

Table 4

Chemical compositions of the filtrates measured by ICP-OES technique and deduced compositions of the solid solutions (see text).

ICP-OES analyses	Ti ions (g.l ⁻¹)	Al ions (g.l ⁻¹)	Cu ions (g.l ⁻¹)	Solid solution composition
Filtrate after treatment at 760 °C	0.0030 ± 0.0005	0.0022 ± 0.0005	0.0109 ± 0.0005	[Ti _{0.85} Cu _{0.15}] ₂ Al _{0.75} Cu _{0.25} C
Filtrate after treatment at 800 °C	0.0053 ± 0.0005	0.0102 ± 0.0005	0.0820 ± 0.0005	[Ti _{0.85} Cu _{0.15}] ₂ Al _{0.58} Cu _{0.42} C

solid solution is dissolved by HNO₃.

After chemical etching, considering that the totality of the metals is dissolved, the filtrate contains:

$$n(\text{Cu ions}) = [n' - nx - 2ny + n\tau(2y + x)]$$

$$n(\text{Ti ions}) = [2ny + 2n\tau(1 - y)]$$

$$n(\text{Al ions}) = [nx + n\tau(1 - x)]$$

where,

n: initial Ti₂AlC mole content

n': initial Cu mole content

x: substitution rate of Al by Cu

y: substitution rate of Ti by Cu

τ: dissolution rate of the MAX phase solid solution.

Moreover, in order to calculate the composition of the solid solution, one has to consider the impurities that are not dissolved in the filtrate. If these impurities were dissolved in the filtrate, the solution should contain:

$$n(\text{Cu ions}) = [n' - nx - 2ny + n\tau(2y + x)]$$

$$n(\text{Ti ions}) = [2ny + 2n\tau(1 - y)] + n_{\text{TiAl}} + 3n_{\text{Ti3Al}} + n_{\text{TiC}} + 2n_{\text{Ti2Al5}} + 3n_{\text{Ti3AlC2}}$$

$$n(\text{Al ions}) = [nx + n\tau(1 - x)] + n_{\text{TiAl}} + n_{\text{Ti3Al}} + 5n_{\text{Ti2Al5}} + n_{\text{Ti3AlC2}}$$

This system of three equations includes ten known parameters: n and n' (the mole content of MAX phase and Cu initially introduced), n (Cu ions), n (Ti ions) and n (Al ions) (the mole content of metallic ions measured in the filtrate using ICP-OES technique) and the mole content of the different impurities (n_{TiC}, n_{TiAl}, n_{Ti3Al}, n_{Ti2Al5}, n_{Ti3AlC2} from Rietveld refinement). Thus, the three unknown terms x, y and τ can be calculated.

Finally, the resolution of the system gives a dissolution rate of Ti₂AlC about zero, which confirms that a very selective chemical etching is performed using nitric acid. The substitution rates of Al by Cu are 25 ± 1 % and 42 ± 6 % whereas the substitution rates of Ti by Cu are 15 ± 1

% and 15 ± 1 % for Ti₂AlC/Cu composites heat-treated at 760 and 800 °C, respectively. The corresponding calculated Cu, Al, Ti and C atomic fractions are given in Table 3. It can be noted that these values are in very good agreement with the ones determined from EDXS analyses in small volumes of the solid solutions obtained at 760 and 800 °C.

4. Conclusion

A new (Ti_{1-y}Cu_y)₂(Al_{1-x}Cu_x)C MAX phase solid solution has been synthesized by thermal treatment performed at 760 and 800 °C for 2 h of a mechanically-milled Ti₂AlC-40 vol% Cu mixture. Experimental evidence of Al atoms substitution by Cu atoms into the crystallographic structure of Ti₂AlC is demonstrated by both XRD and EDXS analyses. EDXS analyses allow determining the composition of the solid solutions synthesized at 760 and 800 °C.

A selective chemical etching has been performed on the (Ti,Cu)₂(Al,Cu)C-Cu(Al) composite obtained after thermal treatment to dissolve the Cu(Al) matrix in order to measure the composition of the solid solution only. Using nitric acid, a very selective chemical etching is performed with a dissolution rate of the MAX phase which is about zero. Such an etching also allows determining indirectly the composition of the MAX phase solid solution from the analysis of the filtrate.

Results obtained by both methods are in very good agreement: the substitution rates of Al by Cu are 25 ± 1 and 42 ± 6 % when thermal treatment is performed at 760 and 800 °C, respectively. However, the substitution rate of Ti by Cu is about 15 % whatever the sintering temperature. One can note that the substitution rate of Al by Cu in Ti₂AlC MAX phase is in the same range as the one (48–51 %) determined in Ti₃AlC₂ MAX phase after thermal treatment at 760 °C; the substitution of Ti by Al seems larger in Ti₂AlC: 15 % to be compared to 3–7 % for Ti₃AlC₂ [29].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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