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Synthesis and characterization of a new $(\text{Ti}_{1-\varepsilon}, \text{Cu}_\varepsilon)_3(\text{Al}, \text{Cu})\text{C}_2$ MAX phase solid solution

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ABSTRACT

A new $(\text{Ti}_{1-\varepsilon}, \text{Cu}_\varepsilon)_3(\text{Al}, \text{Cu})\text{C}_2$ MAX phase solid solution has been synthesized by sintering at 760 °C compacted Ti_3AlC_2 -40 vol.% Cu composite particles produced by mechanical milling. Using XRD and TEM-EDXS, it has been demonstrated that Cu can enter the crystallographic structure of the Ti_3AlC_2 MAX phase, whereas a $\text{Cu}(\text{Al}, \text{Ti})$ solid solution is also formed during thermal treatment. TEM-EELS analyses have demonstrated that Cu is mainly located on the A site of the MAX phase. The composition of the MAX phase solid solution, determined after selective chemical etching of the $\text{Cu}(\text{Al}, \text{Ti})$ matrix, by analyzing the filtrate and the solid phase using ICP-OES end EDXS methods respectively, is $(\text{Ti}_{0.93-0.97}\text{Cu}_{0.07-0.03})_3(\text{Al}_{0.49-0.52}\text{Cu}_{0.51-0.48})\text{C}_2$.

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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]. 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 site thereby allowing the tuning of their electronic, mechanical, optical or thermal properties [11–18]. In these so-called MAX phases, the M_{n+1}X_n layers, characterized by mostly strong covalent M–X bonds, are interleaved with A layers through 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. Early work on these materials has been focused on their unique mechanical properties, including

strength, ductility, thermal conductivity, resistance to oxidation, etc [9]. Later studies have explored, e.g. reversible deformation [19] and stability of nanosheets upon exfoliation [20–24]. Among the most investigated applications to date are: (i) the use in future nuclear power plants [25], (ii) the realization of ohmic contacts on wide gap semiconductors, to achieve high quality devices using Ti-based MAX phase compounds [26–29]. Moreover, because of the combination of their nanolaminated structure and versatile chemistry, these materials were also shown to exhibit promising properties as magnetic inherent nanolaminates [30], and are precursors for a new class of two-dimensional materials, the MXenes [31–33]. Indeed, after the pioneering work of Barsoum et al. on the topotactic transformation of Ti_3SiC_2 by out-diffusion of Si in molten cryolite [34], 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 [35,36]. It has also been demonstrated that nanocomposite materials can be formed by intimate reaction between a metallic element and the A layers [37]. 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 [38] and Dezellus et al. have recently demonstrated that Cu atoms can enter the crystallographic structure of the Ti_3SiC_2 MAX phase but the location

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of Cu is not determined [39]. It has been shown recently that solid solution effects are able to induce magnetism [40,41]. It also allows tuning some properties, among which transport properties [17,42]. MXene carbides, nitrides, carbonitrides [31–33] or new MAX phases compounds (such as $(\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n$ with $n=1, 2$ and 3) [43] can also be stabilized using solid solution effects. Thus, 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 [26–29]. Moreover, transition metal-based MAX phase solid solutions are of major interest regarding magnetic nanolaminates applications [30,40,41].

The goal of this study consists in expanding the family of MAX phase solid solution and more specifically in demonstrating that alloying Ti_3AlC_2 with Cu (transition metal with a full d band) is possible through a powder metallurgy route with very good selectivity on the A site.

2. Experimental

Home-made Ti_3AlC_2 and commercial Cu (3–5 μm , 99.9% purity) powders were selected as starting materials. The Ti_3AlC_2 MAX phase used in this work was synthesized by sintering a Ti:1.9TiC:Al powder mixture using the procedure described in [44]. The porous as-synthesized bulk Ti_3AlC_2 was crushed into powder in order to obtain particles whose sizes are in the range 80–200 μm . In order to prepare homogeneous Ti_3AlC_2 -40 vol.% Cu mixtures, Ti_3AlC_2 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, with a ball-to-powder mass ratio of 5:1. Thus, a green sample was produced by cold-compaction using an uniaxial pressure of 300 MPa. The green compact was sintered at 760 °C during 2 h under argon atmosphere; the heating and cooling rate were fixed at 10 °C/min.

After sintering, the samples were grinded using SiC papers and then polished with a diamond suspension. Finally, a chemo-mechanical polishing has been performed using a neutral suspension of alumina nanoparticles. Such a chemo-mechanical polishing allows to produce a very flat surface and to avoid any work hardening due to conventional grinding.

The microstructure of the Ti_3AlC_2 and Cu co-milled powders as well as the microstructure of the sintered end-product were examined using a high resolution, Field-Emission Scanning Electron Microscope (FESEM Jeol 7001F-TTSL) coupled with Energy-Dispersive X-ray Spectrometry (EDXS, Oxford Energy) for chemical analyses.

Phase identification was performed by X-Ray Diffraction (XRD) using a Bruker D8 diffractometer with $\text{Cu-K}\alpha_1$ radiation. XRD data were refined using the Materials Analysis Using Diffraction (MAUD) [45] software to extract the lattice parameters (LP) and the volume content of the different phases. Microstrains and grain sizes for the different phases were also refined using Popa rules [46].

Transmission Electron Microscopy (TEM, Philips CM20) equipped with EDXS analysis (Bruker) was used to perform chemical and structural analyses at the grain scale on the sintered end-product. Thin foils for TEM observations, were prepared by a slow mechanical polishing down to 20 μm prior to being argon ion thinned with a Precision Ion Polishing System (PIPS) from GATAN. Note that a Mo grid was used to avoid any artifact in the Cu signal.

For the Electron Energy-Loss Spectroscopy (EELS) experiments, the heat-treated samples were scratched using a diamond tip to get a small amount of powders. These powders were hand milled before being collected on a holey carbon grid. EELS spectra were recorded on thin areas (thickness <50 nm) on the border of micro-

Table 1

Lattice parameters of the Ti_3AlC_2 and Cu phases and height of the Ti2 atoms in the unit cell of the MAX phase.

	Ti_3AlC_2		Cu	
	a (Å)	c (Å)	z_{Ti}	a (Å)
After milling	3.0757(2)	18.554(1)	0.127(1)	3.615(1)
After sintering	3.093(1)	18.649(1)	0.135(1)	3.644(1)
After Cu etching	3.094(1)	18.670(1)	0.134(1)	

scopic grains, the probe size being on the order of 100 nm. Given the nanolaminated structure of the MAX phases, most of the grains were oriented along the [0001] zone axis. TEM-EELS experiments were performed in a JEOL 2200 FS microscope operating at 200 kV and equipped with an in-column omega filter. The energy resolution determined from the zero-loss peak full width at half maximum (FWHM) was 0.8 eV. Spectra were dark count corrected and deconvoluted from multiple scattering using a Fourier-ratio technique [47]. Spectra were recorded in almost parallel illumination and using a 7.5 mRad semi-collection angle β .

A selective chemical etching, with nitric acid (68 wt%), has been performed during 15 min on the sintered 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 has been analyzed using an Inductively Coupled Plasma-Optic Emission Spectrometer (ICP-OES, Perkin Elmer Optima 2000 DV) whereas the solid phase has been weighted and further characterized by XRD and FESEM technics.

3. Results and discussion

3.1. Composite particles obtained after ball-milling

Fig. 1(a) shows the XRD pattern of the Ti_3AlC_2 -40 vol.% Cu composite particles after mechanical milling in the vibratory ball-mill. No peaks other than those of the Ti_3AlC_2 and Cu starting reactants are observed in the XRD pattern of these vibratory milled blends, demonstrating that mechanical alloying does not occur during the milling step.

A representative back-scattered SEM image, performed on the cross-section of a composite particle produced by high energy ball milling, is shown in Fig. 2(a). MAX phase corresponds to the dark contrast and Cu to the bright contrast. No third phase is observed using EDXS analyses, confirming XRD results. Moreover, the SEM image shows that ball-milling of Ti_3AlC_2 and Cu powders leads to the formation of aggregates composed of alternative layers of MAX and Cu phases. As observed in Fig. 2(b), the composite particles have an intimate sandwich-type microstructure characteristic of the fracture, deformation and welding events occurring during mechanical milling [48,49].

3.2. End-product obtained after sintering

The XRD pattern of the sintered end-product is shown in Fig. 1(b). Ti_3AlC_2 and Cu phases detected after ball-milling are still the only structures present after heat treatment. When comparing Fig. 1(a) and (b) (before and after sintering respectively), the strong vanishing of the (002) diffraction peak from the MAX phase can immediately be observed. On the contrary, the (006) diffraction peak intensity, which was quite low prior to the sintering process, appears to be high in Fig. 1(b). Furthermore, a shift towards lower angles of the diffraction peaks of both phases is observed. LP of the different phases were deduced from Rietveld refinement of the XRD patterns (see Table 1). Better refinements were obtained with two copper phases with different LP: for the first phase, the LP correspond to the standard value of copper (3.6149(1) Å) whereas for the

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