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## Experimental evidence of copper insertion in a crystallographic structure of $Ti_3SiC_2$ MAX phase

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### Abstract

Chemical interaction of  $Ti_3SiC_2$  substrate with silver-copper (Ag-Cu) melt is studied after several minutes of contact at 800 and 900°C. Experimental evidence of Cu insertion into the crystallographic structure of  $Ti_3SiC_2$  is given both by X-ray energy dispersive spectroscopy (composition is about  $Ti_{47}Cu_8Si_{13}C_{32}$ ) and by electronic diffraction patterns obtained by transmission electronic microscopy for single grains. Moreover, the X-Ray diffraction pattern shows that insertion of Cu induces a slight increase in the lattice parameters and a modification of peak intensities.

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MAX phases have attracted much attention recently because these compounds combine some of the best attributes of both ceramics and metals. For example,  $\text{Ti}_3\text{SiC}_2$  has excellent oxidation resistance, high elastic modulus and strength, chemical stability, excellent thermal shock resistance, good machinability and a high ratio of fracture toughness to strength [1]. This unique combination of properties associated with a low density makes MAX phases interesting principally in the sustainable development field: their resistance to environmental effects should lead to a longer life-time and their low density to a decrease in energy consumption. Thanks to their chemical stability and high electrical and thermal conductivities, the potential applications include the replacement of Ni-based alloys for structural materials [2], use as a contact layer on SiC substrate for high temperature microelectronic devices, heating elements for furnaces, non-oxidizing plugs for replacing gold-plated plugs, etc [3–6].

Since the discovery of graphene, two-dimensional structures have become an attractive research area [7]. It is expected that these particular structures will provide a wide range of unique properties to stimulate active research into possible device applications. After the pioneering work of Barsoum et al. on the topotactic transformation of  $\text{Ti}_3\text{SiC}_2$  by diffusion of Si in molten cryolite [8], Naguib et al. recently demonstrated that MAX phases can be considered as precursor materials to produce two-dimensional carbides with a more complex chemistry, and therefore with the possibility of finely tuned properties, by simple exfoliation of the A atom layer [9,10]. By extension, it is also to be expected that nanocomposite materials can be formed by intimate reaction between a metallic element and the A layers [11–13].

Dezellus et al. have shown that the wetting behavior of an Ag-Cu eutectic melt on the deoxidized surface of  $\text{Ti}_3\text{SiC}_2$  is very similar to a non-reactive metal-to-metal wetting [12]. Nearly perfect wetting is illustrated by both a deep infiltration of the liquid along the grain boundaries of a HIP-  $\text{Ti}_3\text{SiC}_2$  substrate, and a high spreading velocity on the free surface of about  $70 \text{ mm}\cdot\text{s}^{-1}$ . Moreover, spreading is accompanied by (but not coupled with), a strong reactivity between Cu and  $\text{Ti}_3\text{SiC}_2$ , and the substrate was therefore observed to be modified. The aim of the present study was to conduct a detailed characterization of this interaction between Cu and  $\text{Ti}_3\text{SiC}_2$  between  $800^\circ\text{C}$  and  $900^\circ\text{C}$  during short-duration heat treatment, using different experimental techniques such as X-ray diffraction (XRD), X-ray energy dispersive spectroscopy (XEDS) and transmission electron microscopy (TEM). This subject is of interest as the chemical interaction between Cu and  $\text{Ti}_3\text{SiC}_2$  (and more generally with 312 MAX phases) is a key parameter either for brazing applications [14–17] or for the synthesis of Cu-base metal matrix composites reinforced by  $\text{Ti}_3\text{SiC}_2$  particles [18–21].

The experiments were performed using  $\text{Ti}_3\text{SiC}_2$  substrates provided by 3-ONE-2 LLC [22]. It should be noted that two significant impurity phases were detected by XRD analysis: TiC (approximately 15 wt.%) and  $\text{TiSi}_2$  with a lower content. This was due to the unavoidable deviation from homogeneity when large batches of powders are processed. The substrate surface was polished down with a  $1 \mu\text{m}$  diamond paste, thus giving rise to an average roughness value,  $R_a$ , of approximately a few hundred nanometers. The experiments were conducted in a metallic furnace under vacuum (about  $5 \times 10^{-5} \text{ Pa}$ ) obtained with a rotary pump and an oil diffusion pump,

each equipped with a liquid nitrogen trap. First, the Ag-Cu eutectic alloy was melted in an alumina crucible placed above the  $\text{Ti}_3\text{SiC}_2$  substrate by heating pure Cu and Ag (99.999wt.%) [11]. Before the spreading experiments, the solid substrate was deoxidized by heat treatment under vacuum at 850°C for 30 min prior to deposition of the liquid droplet. The liquid droplet was deposited by pushing out the liquid alloy through the alumina crucible down to the substrate. Two spreading experiments were carried out: the first at 800°C and the second at 900°C. After deposition and instantaneous spreading of the Ag-Cu droplet, isothermal contact between the solid substrate and the Ag-Cu melt was maintained for 7 min (420s) at 800°C. The purpose of this experiment was to observe modifications in the  $\text{Ti}_3\text{SiC}_2$  after short-duration heat treatment. In the second type of spreading experiment (at 900°C), the isothermal contact between the solid substrate and the Ag-Cu melt was maintained for 30 min in order to observe possible variations in  $\text{Ti}_3\text{SiC}_2$  modification.

After cooling, a section of the solidified droplet and substrate was cut with a diamond saw, embedded in resin and polished down with a 1 $\mu\text{m}$  diamond paste. Microstructural observations and microanalyses were performed by scanning electron microscopy (SEM) on a FEI Quanta 250 FEG instrument equipped with a silicon drift detector (SDD) to perform X-ray energy-dispersive spectroscopy (XEDS) analysis. X-ray diffraction patterns were also recorded on the substrate surface (ex-liquid/solid interface) after elimination of the droplet by careful and progressive grinding on SiC paper. This pattern can be compared to that recorded on the as-received  $\text{Ti}_3\text{SiC}_2$  substrates. Finally, TEM samples were also machined from the solidified droplet after elimination of the droplet and the unmodified rear face of the  $\text{Ti}_3\text{SiC}_2$  substrate by grinding on SiC paper followed by Ar ion milling. The TEM study was conducted on the resulting thin foils using a 2010 JEOL microscope running at an accelerating voltage of 200 kV and equipped with the XEDS INCA Energy TEM 100X device.

Figure 1 presents a backscattered SEM image of the interface after a wetting experiment at 800°C for a contact time of 420s between the liquid and the solid phase. Good wetting was observed with a final contact angle as low as 10° after a spreading time of less than 40ms. Good wetting is also highlighted in Figure 1 by the infiltration of the substrate by the liquid along the grain boundaries. Note that nearly perfect wetting is not associated with the formation of a reaction layer at the interface between the substrate and the Ag-Cu alloy. However, the backscattered micrographs (Figure 1) show that  $\text{Ti}_3\text{SiC}_2$  grains up to 40 microns below the surface are characterized by a lighter shade of grey than the original grains, indicating a change in their composition. Preliminary results reported in [12], based on an Electron Probe Micro Analysis (EPMA), showed the presence of Cu in the modified grains. These results were confirmed by XEDS analysis performed in a SEM Quanta FEI 250 FEG equipped with an SDD detector. Quantitative information was obtained by comparing the characteristic X-ray intensity of each element present in the specimen with the intensity of the same radiation emitted by a standard material of known concentration. The concentration of each element in the specimen is calculated from the ratio between specimen and standard material intensities using the PAP model [23]. Pure Ag, Cu, Si, Ti and C elements were used as physical standards and the IDFIX system of SAMX microanalysis was

used to perform PAP corrections. The average composition and composition uncertainties of the two types of  $\text{Ti}_3\text{SiC}_2$  grains, modified (lighter grey) and unmodified, are respectively:  $\text{Ti}_{47}\text{Cu}_8\text{Si}_{13}\text{C}_{32}$  and  $\text{Ti}_{50}\text{Si}_{17}\text{C}_{33}$  (see table 1).

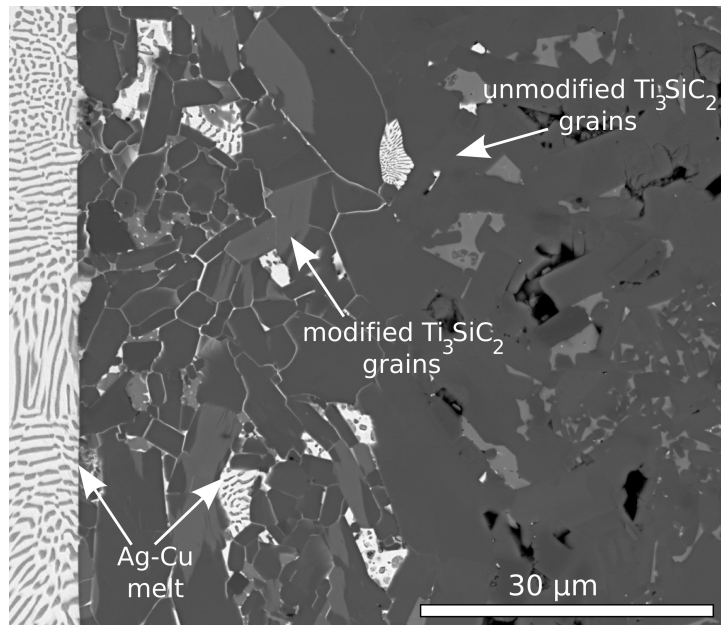


Fig. 1: SEM backscattered micrograph representing a cross-section of the interface between an Ag-28wt.%Cu eutectic alloy and a  $\text{Ti}_3\text{SiC}_2$  substrate after prior deoxidizing heat treatment of the substrate at 850°C and a subsequent contact time with the liquid of 420 s at 800°C.

However, considering the interaction volume for analyses performed with 15kV electron beam acceleration, the XEDS results average the composition over a typical volume a 1 cubic micrometre. Therefore, the composition can be either the composition of a modified  $\text{Ti}_3\text{SiC}_2$  phase with inserted Cu, or an average composition of an intimate two-phase mixture between  $\text{Ti}_3\text{SiC}_2$  and a Cu-rich phase. To overcome this difficulty, XEDS analyses were also performed on a TEM specimen taken from the substrate near the interface, after removal of the metallic droplet and the rear face of the  $\text{Ti}_3\text{SiC}_2$  substrate. This characterization was carried out on a second type of wetting specimen, after spreading at 900°C and a total contact time between liquid and solid of about 30min.

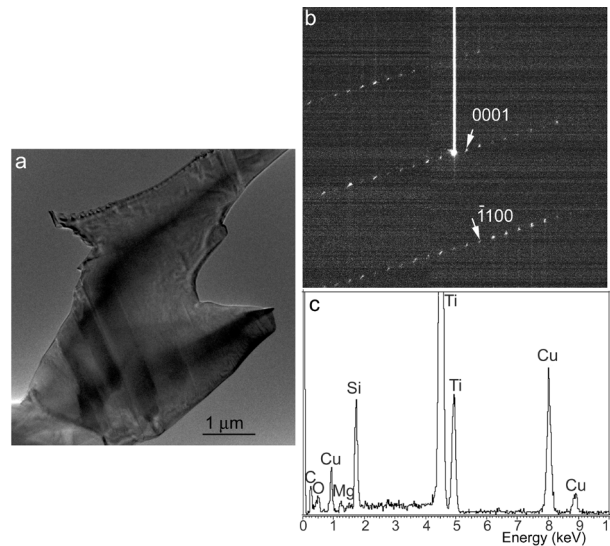


Figure 2: (a) TEM micrograph of a modified  $\text{Ti}_3\text{SiC}_2$  grain. (b) Diffraction pattern of the grain viewed along the  $\langle 11-20 \rangle$  zone axis. (c) XEDS spectrum of the grain revealing the presence of Cu inside the modified  $\text{Ti}_3\text{SiC}_2$  grain.

Figure 2c presents a typical XEDS spectrum for modified  $\text{Ti}_3\text{SiC}_2$  grains during TEM characterization and reveals the presence of Cu inside the grains. Note that a beryllium sample holder was used to avoid any artifact in the Cu signal. The average compositions obtained by TEM-XEDS are compared with the XEDS analysis results from the SEM characterizations in table 1. Note that the carbon content determined by TEM-XEDS is indicative as no absorption correction was used for this light element to take account of the foil thickness. Moreover, no standard specimens were used to define with accuracy the Cliff-Lorimer factors to get quantitative analyses. So the results are mostly qualitative to emphasize the different compositions of the grains. Note the presence of a very small amount of Mg that is identified as pollution coming from the apparatus used for the final ion milling of the sample.

Nature of the grains	SEM / TEM	Ti (at.%)	Si (at.%)	C (at.%)	Cu (at.%)
Ti <sub>3</sub> SiC <sub>2</sub> unmodified	SEM	50	17	33	-
	TEM	51	13	35	1
Ti <sub>3</sub> SiC <sub>2</sub> modified	SEM	47	13	32	8
	TEM	45	8	37	10

Table 1: Typical compositions of Ti<sub>3</sub>SiC<sub>2</sub> grains after XEDS analysis performed during SEM or TEM characterizations. In the case of TEM, a beryllium sample holder was used to avoid any artifact in the Cu signal. The small Cu content (1 %) found in unmodified grains by TEM-XEDS is attributed to Cu redeposition on the thin foil in the PIPS chamber during Ar ion milling.

The concomitant structural (Figure 2b) and compositional analyses (Table 1) of single grains of modified Ti<sub>3</sub>SiC<sub>2</sub> phase confirm the analyses performed by SEM-XEDS and give a clear indication that Cu is present inside the structure of the MAX phase. The extent of the light grey area of modified Ti<sub>3</sub>SiC<sub>2</sub> grains in Figure 1 can be used to evaluate the diffusion coefficient of Cu atoms inside the MAX phase structure. With an extent of about 10 microns in 400 s, the apparent diffusion coefficient of Cu can be estimated as about  $10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ . This value is unusually high for a solid state phenomenon and should be related to the lamellar structure of the MAX phase. From the diffraction patterns on selected areas, the insertion of Cu into the structure is not associated with a significant modification of the crystal structure or of its cell parameters. In order to characterize more precisely any possible modification of the crystallographic structure associated with Cu insertion, X-Ray diffraction (XRD) was used on an as-received 3ONE2 Ti<sub>3</sub>SiC<sub>2</sub> substrate and on the surface of a substrate after the wetting experiment (30 min of interaction with the liquid at 900°C) and careful removal of the droplet. The two XRD patterns recorded in Bragg-Brentano configuration are compared in Figure 3. Note that to facilitate the comparison, the backgrounds have been removed and the patterns have been normalized with reference to the 104 peak that is the expected more intense diffraction peak for Ti<sub>3</sub>SiC<sub>2</sub> [24]. The first observation is the presence of the same secondary phases as in the as-received Ti<sub>3</sub>SiC<sub>2</sub> substrates, namely TiC and TiSi<sub>2</sub>. Moreover, additional Ag-rich and Cu-rich fcc solutions are identified by XRD after the wetting experiments. These metallic phases correspond to the thin solidified liquid layer infiltrated along the substrate grain boundaries.

Concerning the Ti<sub>3</sub>SiC<sub>2</sub> phase the P63/mmc structure is maintained and an increase in both cell parameters was observed: *a* increases from 0.30607 to 0.30683 nm (0.25%) while *c* goes from 1.76235 to 1.76859 nm (0.35%). In parallel with this increase in cell parameter value, a change in peak intensities was also observed, as shown in Figure 3: the diffraction peak intensities of (00l) planes are significantly decreased by 72% for 002 and 26% for 0012. At the same time the intensity of the (110) plane was found to increase by a factor 1.14.

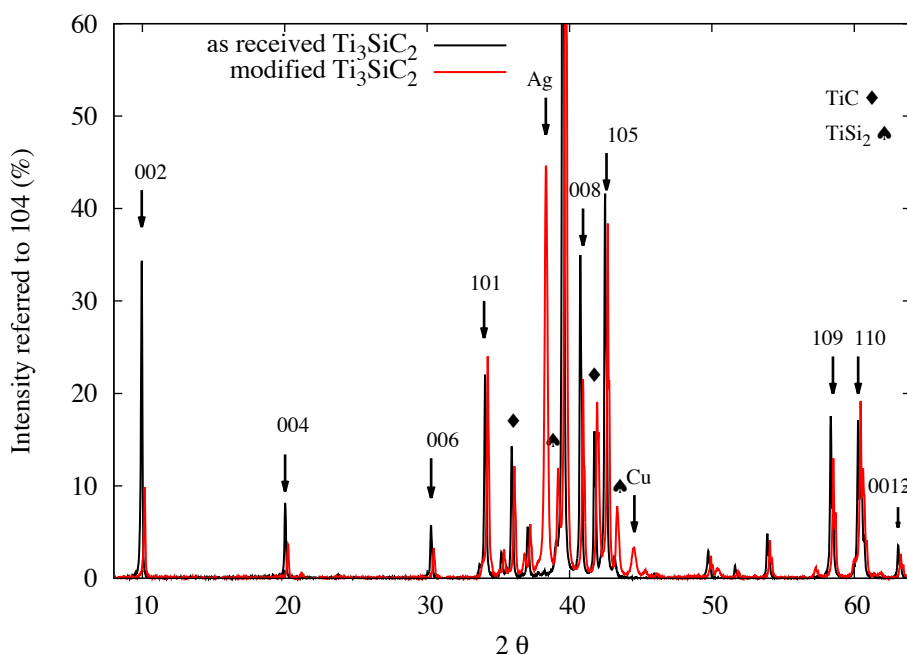


Figure 3: Comparison of X-Ray diffraction patterns recorded in Bragg-Brentano configuration on Ti<sub>3</sub>SiC<sub>2</sub> as received (black line) and after 30 min of interaction with an Ag-Cu eutectic alloy at 900°C. Backgrounds have been removed and each pattern has been normalized with reference to the (104) peak as the 100% intensity peak.

In summary, it has been demonstrated that Cu can enter the crystallographic structure of the Ti<sub>3</sub>SiC<sub>2</sub> MAX phase. Experimental evidence is given both by XEDS (composition is about Ti<sub>47</sub>Cu<sub>8</sub>Si<sub>13</sub>C<sub>32</sub>) and by electronic diffraction patterns obtained by TEM for single grains of the MAX phase with Ag-Cu melt. Moreover, the X-Ray diffraction pattern shows that insertion of Cu induces a slight increase in the lattice parameters and a modification of peak intensities.

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