1628 Microsc. Microanal. 25 (Suppl 2), 2019
doi:10.1017/S1431927619008870

Ti-based MXenes: Preparation by Ion Beam Sputtering and Microstructural Evolution by Ion Irradiation

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MXenes [1] are two-dimensional inorganic compounds (with M as a transition metal and X as C or N) consisting of few-atoms thick layers with graphene-like structure that can, in general, be exfoliated from the parent MAX phases [2]. MXenes can adopt structural forms described by the nomenclature $M_{n+1}C_n$ for n = 1, 2, 3. They are usually produced from the MAX phases by selective etching-out the A element (from the group 13 or 14 of the periodic table). MXenes (as well as MAX phases) have unparalleled properties that can be utilized in various extreme applications. They exhibit a rare combination of good electronic conductivity and hydrophilicity that render them suitable for a wide range of potential applications (e.g., in energy storage, electromagnetic shielding/absorption, nanocomposite fillers, etc.).

In this report, we have utilized a new Low Energy Ion Facility (LEIF), assembled recently in the NPI research infrastructure [3], for adaption of the ion beam sputtering technique (IBS). The LEIF provides an intense ion beam with energy 100 eV – 35 keV and high current up to 500 μA. These are optimal parameters for the efficient IBS technique. Using IBS with a successive thermal processing in vacuum, a series of thin films of Ti-based carbides (including MXenes) have been synthetized. Besides synthesis of samples, the LEIF facility was also applied for ion beam modification of the films.

The microstructure of the synthetized and ion-beam modified samples was inspected by microscopic techniques (performed mainly at UIC Chicago), i.e., SEM and HRTEM/SAED/EDS HRTEM, the chemical composition and the depth profiles of elements were analyzed (at NPI) by the IBA techniques, i.e., RBS and Nuclear Resonance Analysis.

The IBA inspection confirmed stoichiometric ratio of the Ti and C phases, however also oxygen in the system was also found. This was ascribed to oxidation of he spare Ti atoms in the carbide films. In Fig. 1a a thin Ti-based composite, synthetized by IBS (25 keV Ar^+ / 400 μA) and annealed for 6 hours at 600 °C, is depicted. The as-deposited Ti-based carbides represent a mixture with amorpous and crystalline parts. In Fig. 1b is shown a crystalline area that corresponds to the cubic TiC (with $d_{(200)}$ = 0.217 nm, Space Group Fm-3m, PDF card No. 03-65-0803). Besides TiC, however, also other carbide system units, including MXene Ti_2C and others, have been confirmed. Fig. 2 points out how the massive ion beam bombardment affetcs the microstructure of the Ti-based carbide films. The irradiation was performed with the 30 keV Ar^+ ions (with a low 100 nA current) up to the fluence 10^{15} cm^{-2}. As can be seen, the irradiation resulted in fabrication of the nanocrystals (Fig. 2a) and mainly formation of a laminar microstructure with ultra-thin sheets (Fig. 2b).

One can conclude that by IBS, thin films of Ti-based carbides (including MXenes) can be synthetized. Ion beam irradiation of the films has a profound effect – crystallization and laminar structure formation [4].

References:

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[3] http://canam.ujf.cas.cz (accessed 02, 22, 2019).
[4] The authors acknowledge funding from the GACR, Czech Republic, Project No. 18-21677S.

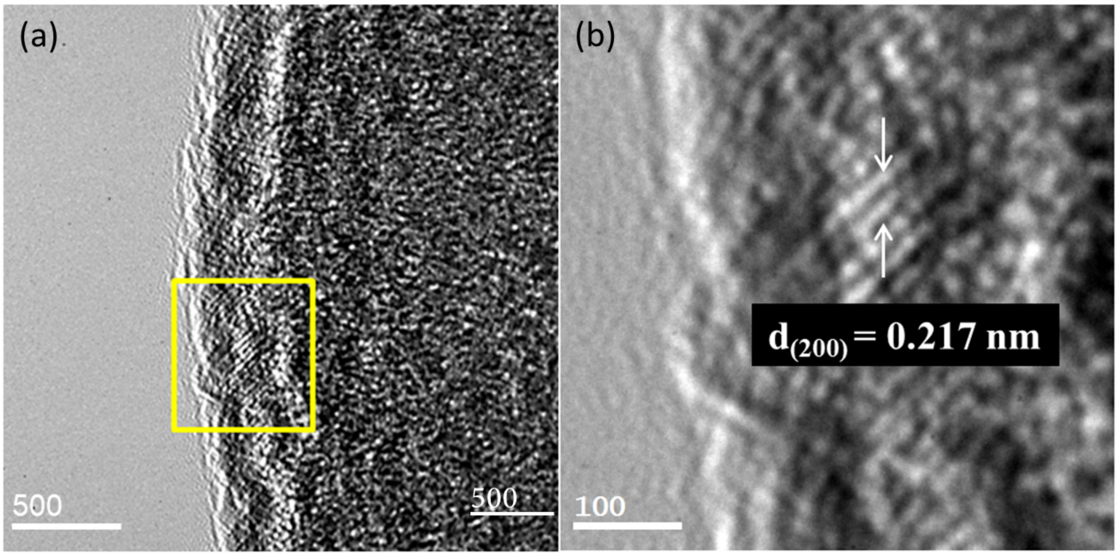

Figure 1. Thin composite of Ti and C phases, synthetized (with a stoichiometric ratio Ti:C = 2:1) by IBS (25 keV Ar^+ / 400 μA) with successive thermal annealing (600 °C / 6 h). The film represents a mixture of amorphous and crystalline parts (a). The crystallite in Fig. 1b corresponds to a TiC phase.

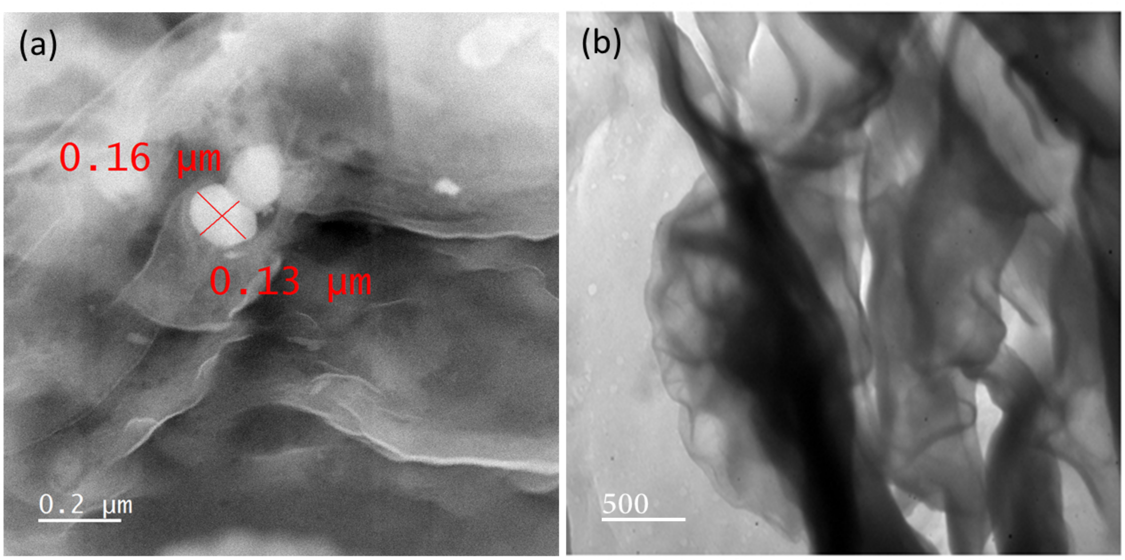

Figure 2. The Ti-based carbide after bombardment by 30 keV Ar^+ ions up to fluence 10^{15} cm^{-2} (a). The ion irradiation had a profound effect – fabrication of the Ti_2C nanocrystals (a) and formation of a laminar microstructure with ultra-thin sheets (b).

https://doi.org/10.1017/S1431927619008870 Published online by Cambridge University Press