doi:10.1017/S1431927618001277
Microsc. Microanal. 24 (Suppl 1), 2018

The Morphology of Ti_2AlC (M_2AX) and Ti_2C (MXene) Sheets Revealed by HAADF STEM Analysis

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The MAX phases are a family of materials composed of a transition metals (M), an A group element (A), and carbon and/or nitrogen (X) with a combination of metallic and ceramic properties [1]. The significance of the MAX phases stems from their laminated structure, where $M_{n+1}X_n$ sheets are interleaved with atomically thin A layers. The M-X bonds consist of a mixture of covalent, metallic, and ionic bonds making M-X compounds exceptionally strong and hence appealing for new applications [2]. The family of graphene-analogous material, known as MXenes, was discovered recently by Barsoum´s group [3]. The MXenes are synthesized from the MAX phases by removal of A-layers through chemical etching, resulting in stand-alone 2D sheets. It was confirmed that the properties of the MXene layered compounds such as wetting, electrical and electrochemical properties can be tunable through selections of surface functional groups. As modified surfaces make MXenes interesting in multiple fields, for instance in energy storage systems and catalysis.

In this study, the structural properties of individual Ti_2C (MXene) sheets are investigated at the atomic level by STEM-EELS and EDX. The Ti_2C compound was generated through selective etching of aluminum (Al) from of the Ti_2AlC ternary M_2AX. Ti_2AlC was prepared by ball-milling of Ti:Al:TiC reagents in ratio 1:1.1:1 for 24 h using zirconia balls. The mixture was annealed at 1300°C for 2 hrs in argon atmosphere. The sintered compact was converted to a powder by milling. Ti_2C MXene powder was prepared by immersing Ti_2AlC powder in 1M of NH_4HF_2 solution for 2 days [4]. After treatment the suspension was washed several times using deionized water. TEM samples were prepared by crushing the powder and next dispersion in ethanol solution, treated in ultrasound for 5 min. A drop of suspension was placed on a Ni grid. The characterization was performed using the UIC microscope JEOL JEM-ARM200CF TEM/STEM with cold field emission source; CEOS probe aberration corrector, Gatan digital cameras, Oxford Energy Dispersive X-ray Spectroscopy (XEDS) and Gatan Electron Energy Loss Spectroscopy (EELS). EELS intensities were normalized with respect to the Ti peak.

From the observations of lattice fringes, solid state obtained sample revealed to have well-crystallized M_2AX-phase Ti_2AlC structure (Fig.1a). The d=3.3Å of the (10-10) planes were perfectly matched with those of the reported Ti_2AlC [5]. M_2AX phase Ti_2AlC possessed a hexagonal structure in which covalent Ti_2C layers are intercalated with metallic Al layers (Fig.1b). According our STEM experiment the molar ratio of Ti:Al:TiC = 1:1.1:1 led to a stoichiometric Ti_2AlC phase (Fig.1d). Fig.2a shows the HAADF STEM of Ti_2AlC phase etched in NH_4HF_2 results for Ti_2C sheets. It is found atomic Ti-C columns (Fig.2b) to be imaged even for single layer structures. The d=2.0Å of the (1-100) planes were matched with those of Ti_2C. The layer stacking sequence of Ti atoms along the [0 0 0 1] is visible. In conclusion, we confirm that Al containing M_2AX phases could be successfully etched to create M_2Xene sheets [6].

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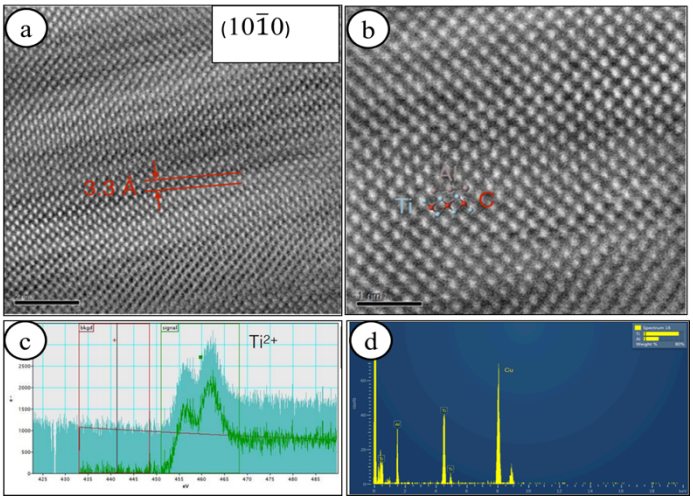

Figure 1. HAADF STEM images of Ti_2AlC samples a) Atomic resolution image of Ti_2AlC b) Crystal structure of Ti_2AlC with its atomic configurations in the unit cell c) $TiL_{3,2}$ fine structure, d) EDS analysis of Ti_2AlC.

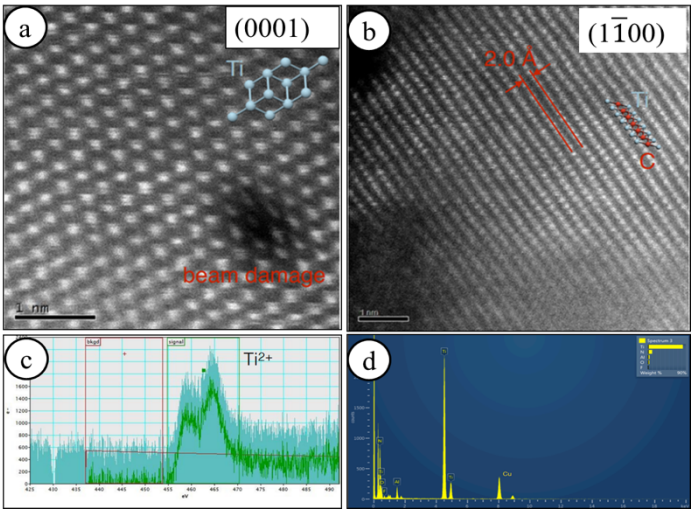

Figure 2. HAADF STEM images of Ti_2C sheets a) A stacking sequence observed in HRTEM images when viewed along the (0001) direction, b) Crystal structure of Ti_2C with its atomic configurations in the unit cell, c) Ti $L_{3,2}$ fine structure and d) EDS analysis of Ti_2C sheets.

https://doi.org/10.1017/S1431927618001277 Published online by Cambridge University Press