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Structure of a new bulk $Ti_5Al_2C_3$ MAX phase produced by the topotactic transformation of Ti_2AlC

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Abstract

Upon annealing cold-pressed Ti_2AlC, −325 mesh powders, at 1500 °C for 8 h in argon, the resulting partially sintered sample contained 43(±2) wt.% of the layered ternary carbide $Ti_5Al_2C_3$. Herein, the X-ray powder diffraction pattern of $Ti_5Al_2C_3$ is reported for the first time and its structure and stoichiometry are confirmed through high-resolution transmission electron microscopy. This phase has a trigonal structure (space group P3m1) with a unit cell consisting of 3 formula units and cell parameters of $a = 3.064$ Å, $c = 48.23$ Å. The lattice parameters determined through first principles calculations agree reasonably well with the experimentally determined values. At 147.1 GPa, the calculated bulk modulus falls between the bulk moduli of Ti_2AlC and Ti_3AlC_2. The transformation from Ti_2AlC to $Ti_5Al_2C_3$ is topotactic.

Keywords: Carbides; Sintering; Electron microscopy; X-ray methods; Powders-solid state reaction

1. Introduction

Binary, early transition metal carbides possess a number of desirable properties including high-temperature stability, high melting point, high hardness, and low compressibility relative to metals; however, their applications are limited because they are brittle, difficult to machine, and highly susceptible to thermal shock. The Ti–Al–C system includes ternary phases that possess ceramic-like properties of their binary relative, TiC, while overcoming many shortcomings of the latter by acquiring some of the more favorable properties of metals. Most notably, two of the ternaries in the system are part of a family of nanolaminated compounds known as MAX phases, which have the general formula $M_{n+1}AX_n$ ($n = 1$–3) where M is an early transition metal, A is an element from groups IIIA or IVA, and X is C or N. They can be further characterized according to their value of n: "2 1 1″ for $n = 1$, "3 1 2″ for $n = 2$, and "4 1 3″ for $n = 3$.

The synthesis of Ti_2AlC was first reported in the 1960s,[1] along with some 3 1 2 phases, including Ti_3SiC_2.[2] Several decades later in 1994, Pietzka and Schuster synthesized Ti_3AlC_2 for the first time and found that it was isostructural with Ti_3SiC_2.[3] It was later discovered that, as a class, the MAX phases have unusual yet attractive and sometimes unique combinations of properties, and these phases have since attracted a great deal of interest.[4–7] They are excellent electric and thermal conductors with exceptional thermal shock resistance. While they are elastically quite stiff, they are also relatively soft and readily machinable, with exceptional damage tolerance.[4,5,8] Some are creep and fatigue resistant.[9–11] Of the > 60 MAX phases known to date, Ti_2AlC and Ti_3AlC_2 are particularly significant when considering the transition of MAX phases from the laboratory to practical applications. They have perhaps the greatest potential for commercialization due to their excellent oxidation resistance and the accessibility of their starting materials, which are relatively inexpensive and readily available.[12,13]

In the Ti–Al–C system, three ternary compounds have been reported to date. Two of them, Ti_3AlC_2 and Ti_2AlC, are MAX phases, which crystallize in a hexagonal lattice (space group $P6_3/mmc$) composed of M–X octahedra stacked between layers of the A element. Another ternary carbide, Ti_3AlC, has a structure similar to oxide perovskites, with Ti and Al forming

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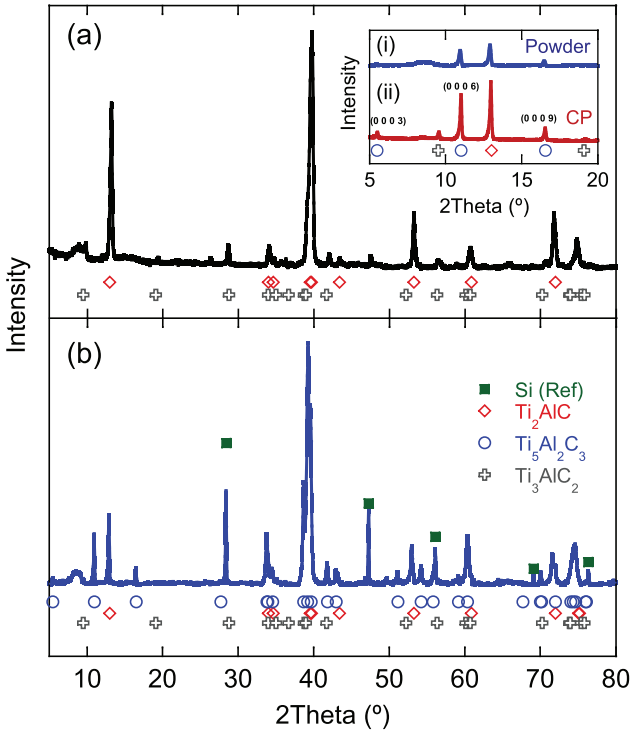

Fig. 1. XRD patterns of Ti_2AlC powder sample, (a) as received and (b) after heat treatment. Inset shows region between $2\theta = 5°$ and 20° for the sample after heat treatment, indexing the (0 0 0 3), (0 0 0 6) and (0 0 0 9) peaks for $Ti_5Al_2C_3$: (i) sample in powder form, and (ii) cold-pressed pellet (CP), where both patterns are normalized to the Si peak at $2\theta = 28.5°$ (not shown). Markers show peak positions for Si (green squares), Ti_2AlC (red diamonds), $Ti_5Al_2C_3$ (blue circles), and Ti_3AlC_2 (gray crosses). XRD patterns are shifted to accommodate markers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

an FCC-like structure and C in the body-centered octahedral hole.[14,15]

Since Ti_2AlC and Ti_3AlC_2 are two of the more promising MAX phases for industrial and commercial uses, the ability to fine-tune their stoichiometry and crystal structure (for example, by altering their stacking sequences) would open more opportunities for engineering their properties. In the present study, we report on the synthesis of a new MAX phase, $Ti_5Al_2C_3$. Its stacking sequence can be considered as alternate layers of Ti_2AlC and Ti_3AlC_2. This phase has previously been reported by Lin et al. as an "intergrown structure" in Ti_2AlC bulk samples[16] and by Wilhelmsson et al. in Ti_2AlC thin films.[17] In both cases, however, it was only observed in small domains through transmission electron microscope, TEM, analysis. Consequently, its X-ray diffraction, XRD, patterns are unknown.

Herein, we show that $Ti_5Al_2C_3$ can be synthesized in bulk. We determine its long-range crystal structure, stacking, and stoichiometry through XRD and TEM analysis. We also perform first principles calculations to determine its ground state parameters and its electronic structure.

2. Experimental details

The sample was made by heating Ti_2AlC powders that were commercially obtained (3-ONE-2, Voorhees, NJ, >92 wt.% purity; particle size <44 μm, i.e., −325 mesh) in an alumina tube furnace under flowing argon, Ar, at 10 °C/min to 1500 °C. The powders were then held at temperature for 8 h. After cooling to room temperature, powders were obtained from the resultant partially sintered bulk piece (relative density of ≈80%) using a titanium nitride coated milling bit.

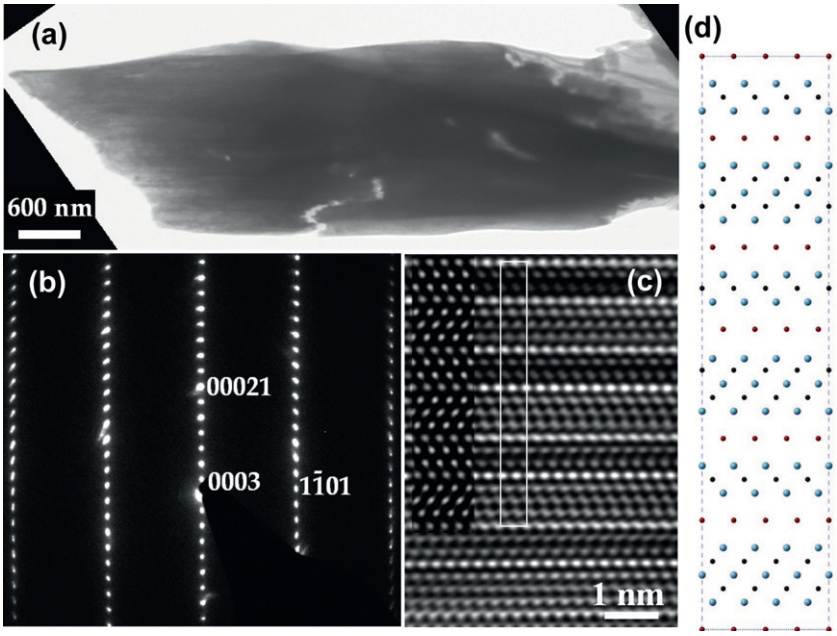

Fig. 2. High-resolution TEM (HRTEM) image of a heat-treated $Ti_5Al_2C_3$ sample: (a) large grain of $Ti_5Al_2C_3$, (b) selected area electron diffraction (SAED) pattern shown parallel to the [1 1 $\bar{2}$ 0] direction, (c) HRTEM image of the [1 1 $\bar{2}$ 0] axis projection showing $Ti_5Al_2C_3$ stacking, and (d) illustration of the [1 1 $\bar{2}$ 0] plane for comparison with highlighted region in (c).