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Cold-pressed α -Ta₄AlC₃ powders are annealed up to 1750 °C to test first-principles predictions of α - β phase-stability reversal at 1600 °C.

The α -Ta₄AlC₃ samples are stable up to 1600 °C, with no indications of any α - β transformation.

Transmission electron microscopy shows zig-zag stacking sequence characteristic of α -Ta₄AlC₃, as well as tantalum oxide impurities.

The XRD patterns suggest that defects such as vacancies or antisites may increase the stability of α -Ta₄AlC₃.

High-temperature Stability of α -Ta₄AlC₃

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Keywords: X-Ray diffraction (XRD); Transmission Electron Microscopy (TEM); polymorphic;

Abstract

Cold-pressed α -Ta₄AlC₃ powders were annealed up to 1750 °C to test first-principles predictions of α - β phase-stability reversal at 1600 °C. Up to 1600 °C, the α -Ta₄AlC₃ samples were stable with no indications of any α - β transformation, as shown by the strong characteristic X-ray diffraction peaks of α -Ta₄AlC₃ and the zigzag stacking observed by transmission electron microscopy. These results show that, in this experimental situation, high temperature alone is not sufficient to cause the α - β transformation.

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1. Introduction

The layered ternary $M_{n+1}AX_n$ ceramics, or “MAX” phases, where M is an early transition metal, A is an A-group element, and X is C or N, crystallize in the space group $P6_3/mmc$ and contain alternate layers that stack along the c direction consisting of octahedral M_6X building blocks that form a zigzag pattern with close-packed A-group atomic mirror planes [1-3]. The MAX phases are classified into 3 groups based on their n values, i.e., “211” for $n = 1$, “312” for $n = 2$, and “413” for $n = 3$. While the 211 and 312 MAX phases have been extensively investigated and characterized, it was long believed that Ti_4AlN_3 was the only 413 MAX phase [4]. Since 2004, however, several new 413 phases have been discovered; first with the synthesis of Ti_4SiC_3 and Ti_4GeC_3 thin films [5-6] and then bulk synthesis of Ta_4AlC_3 in the form of polycrystals [7-10] and single crystals [11]. More recently, the 413 phases V_4AlC_3 [12-13], Nb_4AlC_3 [14], and Ti_4GaC_3 [15] were also synthesized in bulk form.

Of the experimentally identified 413 phases, only Ta_4AlC_3 has shown polymorphism. Manoun *et al.* [10] found large differences between experimental and calculated data in their high-pressure X-ray diffraction study of sintered Ta_4AlC_3 and tentatively attributed this to preferred orientation. Soon afterwards, however, Lin *et al.* showed that their hot-pressed Ta_4AlC_3 structures exhibited a different stacking sequence from the structure of Ti_4AlN_3 [9, 16], explaining the discrepancies observed by Manoun *et al.* In contrast, Etzkorn *et al.* synthesized Ta_4AlC_3 single crystals and found the same stacking sequence to be that of Ti_4AlN_3 [11]. Eklund *et al.* also observed this stacking in Ta_4AlC_3 powder and concluded that there were two Ta_4AlC_3

polymorphs. The two polymorphs are now known as α -Ta₄AlC₃, with Ti₄AlN₃-like stacking sequence, and β -Ta₄AlC₃, in which the Ta_{II} and C_{II} atom positions* are shifted resulting in de-twinning and loss of the normal characteristic zigzag stacking of the TiX₆ layers.

The MAX phases have also shown another type of polymorphism that has been demonstrated in the 312 and 211 phases and involves shearing of the A layers. This type of polymorphism appears to be driven by shear strain under high-pressure conditions and/or TEM sample preparation [3, 17-21]. In Ta₄AlC₃, on the other hand, the polymorphism is most likely thermodynamically driven with structural differences confined to the Ta₄C₃ slabs [3, 7, 9]. A number of recent papers have been published on the polymorphs of Ta₄AlC₃ [2, 22-23]. Since this polymorphism would also be expected in V₄AlC₃ and Nb₄AlC₃, as V and Nb have the same number of valence electrons as Ta, Wang *et al.* [24] performed first principles studies to investigate reasons for this discrepancy. They predicted that a polymorphic phase transformation from α - to β -Ta₄AlC₃ is thermodynamically favorable at 1600 °C, unlike in V₄AlC₃ and Nb₄AlC₃ [24]. The main origin of the predicted decrease in relative free energy from α - to β -Ta₄AlC₃ is the relative strength of the Ta_{II}-C_{II} bond, which is shorter in β -Ta₄AlC₃. In the present study, we experimentally test this prediction by heating cold-pressed α -Ta₄AlC₃ powders to temperatures as high as 1750°C.

2. Experimental Details

Experimental details for the synthesis of the α -Ta₄AlC₃ powder can be found

* In the Ta₄AlC₃ structures, there are two different Ta sites, those adjacent to Al sites, and those not. These sites are referred to herein as Ta_I and Ta_{II}, respectively. Similarly, the two nonequivalent C sites are referred to as C_I and C_{II}.

elsewhere [7]. Approximately 3 g of the as-received powder was cold pressed into a pellet, with a radius of 6.5 mm at 700 MPa. The pellet was embedded in approximately 5.9 g of un-compacted Ta_4AlC_3 powder in a 100 mm diameter alumina crucible. The crucible was placed in an alumina tube furnace with a flowing Ar atmosphere in three successive heat treatments. The first annealing was at 1450 °C for one hour, followed by a second at annealing at 1550 °C also for one hour, followed by one 1600 °C for 2 hours. The heating rate in all cases was constant at 5 °C min⁻¹. Finally the sample was heated in a vacuum, graphite furnace at 8 °C min⁻¹ to 1750 °C for 4 h. The latter furnace was used since the Ar furnace used for the first three runs was limited to 1600 °C. In all cases, the sample was furnace cooled.

X-ray diffraction (XRD) was performed on the as-prepared powder and after each heat treatment in a powder diffractometer using Cu K α radiation. Approximately 10 wt.% Si was mixed by mortar and pestle with the powder samples to normalize peak intensities for comparison. The data was normalized to the Si peak intensities. The simulations of the XRD patterns of Ta_4AlC_3 accounting for defects (vacancies and antisites) were performed using the CaRIne software [25]. The microstructures of the as-prepared and annealed at 1550 °C powder samples were characterized by using a FEI Tecnai G2 TF 20 UT transmission electron microscope (TEM) operated at 200 kV with a 0.19 nm point resolution. The TEM specimens were made by suspending the powder in ethanol and collecting grains on holey carbon grids.

3. Results

Figures 1a, b, c, d, and e show the XRD patterns of the as-received and cold-

pressed Ta_4AlC_3 powder and after annealing at 1450°C, 1550°C, 1600°C, and 1750°C, respectively. All annealed samples up to 1600 °C retain the $\alpha\text{-Ta}_4\text{AlC}_3$ structure. This is obvious from the intensities of the peaks indexed in Fig. 2, as $(10\bar{1}2)$, $(10\bar{1}4)$, $(10\bar{1}6)$ and $(10\bar{1}7)$ peaks. In $\beta\text{-Ta}_4\text{AlC}_3$ the intensities of these peaks are negligible and would have been strongly reduced in intensity had an $\alpha\text{-}\beta$ transformation occurred [7, 26]. Furthermore, the $(10\bar{1}5)$ peak intensity would have significantly increased in intensity had $\beta\text{-Ta}_4\text{AlC}_3$ formed. After the heat treatment at 1750°C, only TaC is observed (Fig. 1e).

While there are no indications of any $\alpha\text{-to-}\beta$ phase transformations, the following systematic observation can be made: the basal reflections decrease in intensity in relation to non-basal ones. This is clear from the (0002) , (0004) , (0006) and (0008) peaks shown in Fig. 1 at approximately $2\theta = 7^\circ$, 15° , 22° , and 29° , respectively, as well as the $(0\ 0\ 0\ 10)$ peak indexed in Fig. 2, which all decrease in intensity relative to the $(1\ 0\ \bar{1}\ l)$ peaks with successive heat treatments.

The as-received powder and the sample annealed at 1550°C were characterized by high resolution TEM. In agreement with the XRD results, these samples were found to contain only the $\alpha\text{-Ta}_4\text{AlC}_3$ phase. Fig. 3a is a HRTEM image along $[11\bar{2}0]$ zone axis of $\alpha\text{-Ta}_4\text{AlC}_3$ from the annealed sample. A magnified image presenting three unit cells is shown in Fig. 3b.

Figures 3c and d show areas of the Ta_4AlC_3 samples where an amorphous tantalum oxide phase was found in the as-received material and that annealed at 1550°C, respectively. The amorphous material consists only of Ta and O, as confirmed

by qualitative EDS. The annealed sample contained significantly more amorphous tantalum oxide than the as-received powder.

4. Discussion

Based on the above results, it is clear that cold-pressed α -Ta₄AlC₃ powder does not transform to β -Ta₄AlC₃ by heat treatment alone as predicted by the *ab initio* calculations of Wang *et al* [24]. Therefore, there must be other factors that drive the α - β phase transformation. First, heating the α -Ta₄AlC₃ samples in the Ar furnace leads to experimental conditions that deviate from the ideal stoichiometry and purity assumed in the *ab initio* calculations. For instance, the presence of secondary phases (e.g. TaC), the possibility of oxidation in the furnace, and the creation of defects such as vacancies are not accounted for in the theoretical predictions. Second, there are significantly more TaO_x impurities in the heat-treated sample (Fig. 3d) compared to the as-received powder (Fig. 3c). Oxidation may thus affect the predicted phase transformation. Third, experimental studies of the β -Ta₄AlC₃ polymorph involve synthesis through hot pressing in addition to higher temperatures [8-10] and the synthesis pressure may also affect the relative phase stability. To test this hypothesis we hot-pressed a stoichiometric mixture of TaC, Al, and graphite powders in a graphite-heated vacuum hot-press at 1500 °C for 2 hrs under a pressure of 70 MPa. Again, the resulting phase was α -Ta₄AlC₃ with unreacted TaC, as confirmed by XRD (not shown).

In support of these arguments, our results show a systematic decrease in basal peak intensity relative to the non-basal peaks with annealing temperature. From simulations of the XRD patterns (Fig. 4), we conclude that these shifts in relative

intensities of basal vs. non-basal peaks can be caused by vacancies on the Ta_I sites or Ta antisite defects on the Al positions. Excess Al (i.e., occupancy greater than 1) would also explain the effect, but the excess would have to be large (30-40%) and is therefore less likely than the other effects. Figure 4 shows that all three types of defects have roughly the same effect on the diffraction pattern, with the intensities of the basal plane peaks decreasing relative to the non-basal peak intensities. Vacancies on Al sites or Ta_{II} sites would have the opposite effect on the XRD patterns. This is interesting, because vacancies on the Al sites would be expected since extended heating at high temperatures results in TaC_x . These results combined with the experimental XRD patterns (Fig. 1) show the possible changes in stoichiometry caused by annealing α - Ta_4AlC_3 and can also be connected to the relative phase stability. While there is no phase transformation, there are indeed systematic changes in the XRD patterns that can be attributed to these possible defects, which may increase the relative stability of the α - Ta_4AlC_3 polymorph.

Summary and Conclusions

No evidence of an α -to- β phase transformation during the annealing of α - Ta_4AlC_3 at temperatures up to 1600 °C was found, contradicting *ab initio* calculations that predict a transformation around 1600 °C. Heating to 1750 °C converts the α - Ta_4AlC_3 to TaC_x . The reason for this apparent discrepancy may be the differences between the idealized conditions for the *ab initio* calculations and non-ideal experimental conditions, including the presence of defects. Heating the powders, however, resulted in a diminution of the relative intensities of the 000 l peaks, which is

likely due to the formation of Ta vacancies or antisites. These results indicate the need for more calculations to study the effects of vacancies, antisite defects, impurities such as oxygen, and pressure on the relative phase stabilities.

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Figure Captions:

Fig. 1: Measured XRD patterns for α -Ta₄AlC₃ powder (a) as-received and after cold-pressing, and successively annealing to temperatures (b) 1450°C, (c) 1550°C, (d) 1600°C and (e) 1750°C. Markers on top of the various peaks denote the phases TaC (X) and Si standard (Δ).

Fig. 2: Detail of the 2θ range 33-44° of the measured XRD patterns for the as-received α -Ta₄AlC₃ (red) and after annealing of 1450°C (blue), 1550°C (green), and 1600°C (black).

Fig. 3: HRTEM of the lattice of α -Ta₄AlC₃ annealed at 1550°C in the $[11\bar{2}0]$ zone axis projection, showing zig-zag pattern stacking sequence typical of α -Ta₄AlC₃: (a) low magnification overview image and, (b) image of three unit cells. (b) and (c) are TEM images showing amorphous TaO_x phase found in as-received Ta₄AlC₃ powder and after annealing at 1550°C, respectively. After the high temperature anneal the volume fraction of TaO_x increases noticeably.

Fig. 4: Simulations of XRD patterns for α -Ta₄AlC₃, (a) perfect crystal, (b) with 30% excess Al, (c) 10% vacancies on the Ta_I sites, and, (d) 10% antisite defects on both Al positions.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 1

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Figure 2
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