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Isothermal Oxidation of Ta₂AlC in Air

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The oxidation behavior, in air, of bulk polycrystalline Ta₂AlC samples was studied in the 600°–900°C temperature range. A protective, essentially X-ray amorphous, oxide layer—which does not appear to be resistant to thermal cycling—forms at 600°C. This layer is comprised of Ta, Al, and O. At 700°C and above, it is compositionally quite uniform, but porous and highly cracked. No phase separation was observed at the micrometer scale. The oxide layers consisted of the crystalline phases, Ta₂O₅ and TaAlO₄, and an X-ray amorphous phase. In the 700°–900°C temperature range, the oxidation kinetics were found to be linear.

I. Introduction

THE ternary carbide Ta₂AlC belongs to a large class of layered solids with the general formula M_{n+1}AX_n, where M is an early transition metal, A an A-group (mostly IIIA and IVA) element, and X is C and/or N (MAX phases). These compounds, with hexagonal symmetry, are built up from M carbide or nitride layers interleaved with pure A element layers. Some of them possess an unusual and sometimes a unique set of properties. They are relatively soft, with Vickers hardness values in the 3–5 GPa range, elastically stiff, electrically and thermally conductive, and readily machinable.^{1,2}

These compounds decompose incongruently in inert atmospheres into MX-based compounds and an A-rich liquid. Typically, their oxidation results in the formation of A- and M-based oxide.^{3–6} Under certain conditions, ternary oxides have been formed.^{3,7} The oxidation can also be accompanied by phase separation in the oxide layers, resulting in the formation of separate, alternating M- and A-rich oxide layers.^{3,5,6}

Recently, Ta₂AlC, among some other MAX phases, has been identified as a possible material for intermediate temperature (550°C) tribological applications.⁸ Before this material can be used in such applications, however, it is imperative to study its oxidation behavior in air. Note, that in inert atmospheres, Ta₂AlC is rather stable. Although its peritectic temperature is unknown, it is higher than 1600°C.

As this is the first report on the oxidation of Ta₂AlC, there are no studies with which to compare our results. It is thus useful to review the behavior of a number of related elements and compounds such as the Ta, Ta₂C, TaC, and the isostructural Nb₂AlC.

Dense bulk TaC and Ta₂C samples, being oxidized at various PO₂ from 0.2 to 1 × 10⁵ Pa in the 700°–850°C temperature range, oxidized notably at temperatures above 700°C. The Ta₂O₅ oxide layers formed were not protective, resulting in an interfacial reaction rate-limited oxidation kinetic presumably at the oxide/substrate interface.⁹ Interestingly, Ta₂C is more resis-

tant to oxidation than TaC. In 5 h at 850°C, 4 mm³ TaC cubes are completely oxidized under PO₂ of 1 atm.

The closest isomorphous analogue to Ta₂AlC, however, is Nb₂AlC. The isothermal oxidation of Nb₂AlC in air in a 650°–800°C temperature range was reported by Salama *et al.*⁷ The oxidation kinetics at 650°C were subparabolic; at 700°C and higher temperatures, the oxidation kinetics were linear, with rates comparable to those for the oxidation of pure Nb.⁷ At 700°C and short oxidation times, the oxidation products were Nb₂O₅ and Al₂O₃. At longer times and/or temperatures greater than 700°C, the products were Nb₂O₅ and NbAlO₄. The layers that formed at 700°C and higher, however, were not protective, resulting in linear oxidation kinetics. There was no evidence of melting of any of the phases formed during oxidation in the temperature range investigated.⁷

Thermodynamically, α- and β-orthorhombic tantalum pentoxides (Ta₂O₅) are the only stable phases at elevated temperatures in air.^{10,11} The low-temperature β-form converts to a higher temperature α phase at ~1360°C. Consequently, β-Ta₂O₅ is the only high-temperature oxidation product obtained when Ta metal is oxidized at 800°C.^{12,13} At lower temperatures (below 500°C), metastable tantalum suboxide phases TaO₃, such as Ta₄O or Ta₂O, form instead, or along with Ta₂O₅.^{10,12,14}

The purpose of this paper is to report on the oxidation behavior of Ta₂AlC in the 600°–900°C temperature range in air. This paper is a continuation of our quest to understand the oxidation kinetics of the more than 50 ternary MAX phases known to exist.^{3,5–7,15,16}

II. Experimental Procedure

The Ta₂AlC sample was prepared by reactive hot isostatic pressing (HIPing) of Ta, Al, and graphite powders (99.9%, Alfa Aesar, Ward Hill, MA). The powders were mixed in stoichiometric proportions by ball milling in a plastic container with alumina balls for 1 h. The mixed powders were sealed in a borosilicate glass tube under a mechanical vacuum, followed by heating at 650°C for 10 h. The collapsed tubes with the pre-reacted powders were HIPed at 100 MPa and 1600°C for 8 h in Ar. After furnace cooling, the encapsulating glass was mechanically removed and rectangular specimens ≈2 mm × 2 mm × 8 mm were cut using a diamond blade. All sides were polished with a 1200 grit SiC paper prior to the oxidation runs.

The oxidation study was carried out using a D-101 CAHN thermobalance. The samples were placed in an alumina crucible, hung by a Pt wire, and oxidized in air between 700° and 900°C for ≈20–40 h. At 600°C, the weight gain was below the detectability level of out balance. At this temperature, the samples were placed in a furnace and intermittently weighed.

X-ray powder diffraction (XRD) data were collected at an ambient temperature on a Siemens D500 diffractometer using CuKα radiation, step scan 0.02°, 1 s per step.

The oxidized samples were mounted, ground, and polished to expose their cross sections. The oxide layer morphologies and thicknesses were measured in a field emission scanning electron microscope (FESEM; Phillips XL30), equipped with an energy-dispersive spectroscope (EDS; EDAX, Mahwah, NJ).

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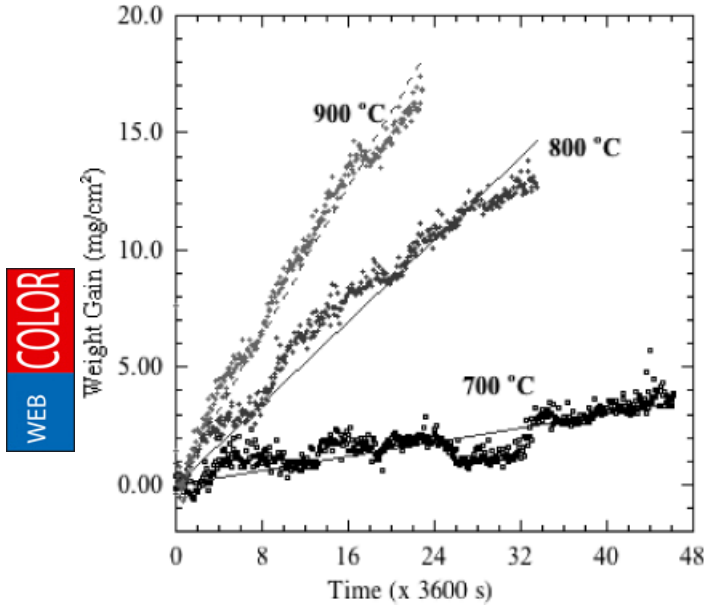


Fig. 1. Normalized weight gain versus time of Ta_2AlC samples isothermally oxidized in air at various temperatures.

III. Results and Discussion

XRD analysis of the Ta_2AlC HIPed samples indicated that they were predominantly single phase, with small amounts of Ta_4AlC_3 , as an impurity phase. All samples were greater than 98% of theoretical density, viz. 11.82 g/cm^3 . At $xx \mu\text{m}$, the grains were small.

The time dependencies of the weight gain during the oxidation of Ta_2AlC in air, in the $700^\circ\text{--}900^\circ\text{C}$ temperature range, are shown in Fig. 1. (The weight gain at 600°C was lower than the sensitivity level of the thermobalance used.) At the higher temperatures, the oxidation rates were linear. The linear reaction rate constants themselves increased almost linearly with increasing temperatures (Fig. 1(b)). This suggests that the oxidation of Ta_2AlC in the given temperature range is limited by a reaction at the oxide/carbide interface.

Analysis of the XRD spectra of surfaces oxidized at 600°C showed the presence of weak lines that corresponded to Ta_2O_5 and AlTaO_4 (Fig. 2). The oxide peaks in the pattern are noticeably broadened, and slightly shifted compared with $\beta\text{-Ta}_2\text{O}_5$, indicating they were poorly crystallized and defective.

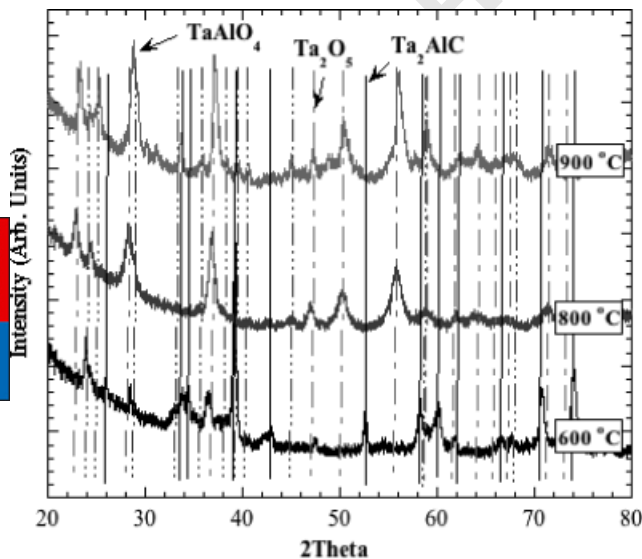


Fig. 2. X-ray diffraction patterns of the Ta_2AlC surfaces after oxidation in air at 600° , 800° , and 900°C for 24 h.

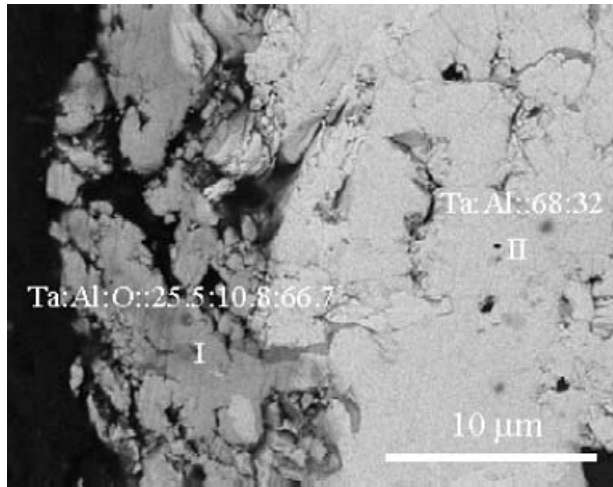


Fig. 3. Cross-sectional backscattered scanning electron micrographs of a Ta_2AlC sample oxidized at 600°C for 40 h. The numbers on the right represent the Ta:Al atomic ratio in the bulk; the ones on the left, the Ta:Al:O atomic ratios in the oxide layer.

After oxidation at 600°C for 40 h, a thin ($<10 \mu\text{m}$) oxide layer was formed (Fig. 3). According to EDS analysis, the Ta:Al:O atomic ratio in the thin oxide layer was $\approx 2:1:6.5$, respectively, which corresponds to the Ta^{5+} and Al^{3+} oxidation states. It follows that it is more likely than not that the protective layer that forms is mostly amorphous. In another experiment, a sample was oxidized for 100 h; no change in the morphology of the oxide layer was noted and no further weight gain was recorded.

However, the presence of the multiple cracks seen in Fig. 3 was not consistent with the passivating nature of the oxide layer. To better understand the origin of these cracks, we thermal cycled a sample by heating it from room temperature to 600°C in air and furnace cooling it five times, while monitoring its weight. The oxidation rate during cycling was roughly an order of magnitude higher than in the isothermal case. We thus conclude that the cracks most probably form during cooling as a result of a thermal expansion mismatch. The thermal expansion coefficient of Ta_2O_5 is reported to be $2.9 \times 10^{-6} \text{ K}^{-1}$ in the $25^\circ\text{--}550^\circ\text{C}$ temperature range and $4 \times 10^{-6} \text{ K}^{-1}$ from 550° to 1200°C .¹⁷ The bulk dilatometric thermal expansion coefficient, TEC, of Ta_2AlC , measured herein, in the $25^\circ\text{--}1000^\circ\text{C}$ temperature range, is $5.7 \times 10^{-6} \text{ K}^{-1}$. It follows that compressive stresses of the order of 450 MPa would develop in the oxide films upon cooling to 600°C . Such stresses, while not excessively high, could be sufficient to compromise the integrity of the thin oxide film, especially as these stresses are in addition to the ones that develop as a result of the oxidation process, viz. reactions (1) and (2).

The XRD spectra of the oxide layers formed at 800° and 900°C are also shown in Fig. 2. According to these results, the oxide layers formed were mainly comprised of $\beta\text{-Ta}_2\text{O}_5$ and AlTaO_4 . Based on the relative intensities of the peaks of these phases, it is fair to conclude that the volume fraction of the AlTaO_4 phase increases with increasing temperature. Note that at all temperatures, the peaks in the XRD patterns are noticeably broadened, implying that the oxide grains formed are quite small.

Cross-sectional SEM micrographs of samples oxidized at different temperatures for different times are shown in Fig. 4. All the oxide layers formed at 700°C and above were porous and highly cracked. Compositionally, however, the oxide layers were rather uniform across their thicknesses. No well-formed grains of separate phases were observed. EDS analysis revealed that the oxide layers formed were fully oxidized and maintained the same Ta/Al atomic ratio within the resolution of our probe spot size of $\sim 1 \mu\text{m}$ as for the matrix.

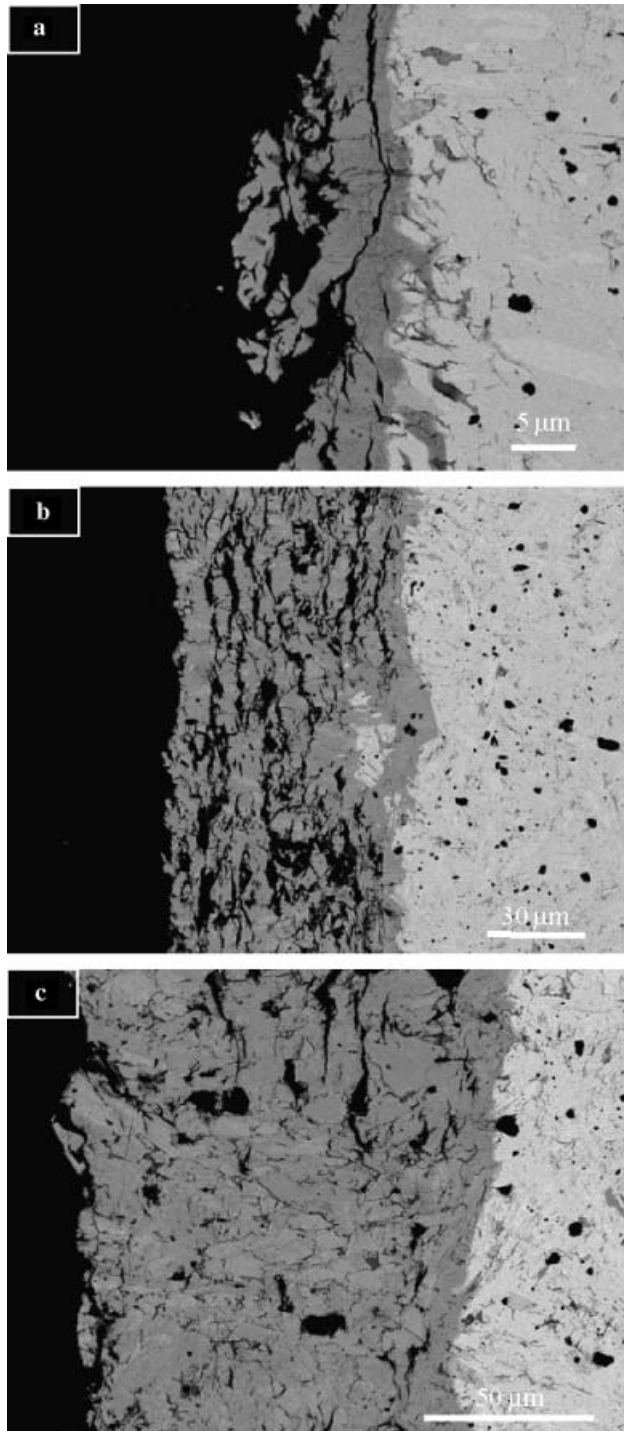
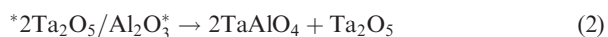


Fig. 4. Cross-sectional backscattered scanning electron micrographs of the Ta₂AlC samples oxidized at (a) 700°C for 46 h, (b) 800°C for 32 h, and (c) 900°C for 24 h.

Based on these results, it is reasonable to conclude that the oxidation of Ta₂AlC occurs according to the following reactions:

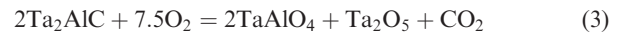


where *2Ta₂O₅/Al₂O₃* designates a micro-constituent that is not necessarily a single phase but could also be multiphase or amorphous. At higher temperatures, reaction (2) is favored. Note that no Al₂O₃ peaks were observed in the XRD spectra. As in all previous work on the oxidation of the MAX phases, the C

is assumed to be completely oxidized. The main evidence is its lack of accumulation at the oxide/carbide interface.^{3,5-7,15,16}

As noted above, this reaction scheme is quite similar to the one that occurs during the oxidation of Nb₂AlC and its solid solutions in air.⁷

Lastly, the cracked and porous nature of the oxides that form at 700°C and above (Fig. 4) are consistent with the linear oxidation kinetics (Fig. 1). The cracks and fissures provide fast diffusion paths for the oxygen toward the reaction interface, as well as the outward diffusion of CO₂. In addition to the thermal expansion mismatches alluded to earlier, another contributing factor to the microcracking is the relative volume change, $\Delta V/V_0$, for the overall reaction:



where V_0 is the molar volume of the MAX phase. For this reaction, $\Delta V/V_0$ is 50%.

IV. Conclusions

The oxidation in air of Ta₂AlC at 600°C results in the formation of a thin protective (at least up to 100 h) oxide layer that prevents further oxidation. The main crystalline phases detected by XRD in this oxide layer were Ta₂O₅ and TaAlO₄, with the balance being X-ray amorphous. The protectiveness of this layer, however, is compromised by thermal cycling.

In the 700°–900°C temperature range, the oxide layers that form are compositionally quite uniform, but porous, highly cracked, and non-protective. They consisted of Ta₂O₅ and TaAlO₄, and some X-ray amorphous phases. The oxidation kinetics were found to be linear at these temperatures.

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