

High-temperature oxidation of Ti₃(Al,Si)C₂ nano-laminated compounds in air

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Abstract

The compound, Ti₃(Al,Si)C₂, was synthesized by hot pressing a powder mixture of TiC_x, Al and Si. Its oxidation at 900 and 1000 °C in air for up to 50 h resulted in the formation of rutile-TiO₂, -Al₂O₃ and amorphous SiO₂. During oxidation, Ti diffused outwards to form the outer TiO₂ layer, and oxygen was transported inwards to form the inner mixed layer.

1. Introduction

The nanolaminated ternary compound, Ti₃SiC₂, consists of Ti₃C₂ octahedrons stacked along the c-axis which are separated by layers of Si atoms. This compound has been extensively studied for a number of applications, due to its unique combination of both metallic and ceramic properties [1]. It is electrically and thermally conductive, easily machinable, ductile with a high stiffness-to-hardness ratio, thermally stable up to at least 1700 °C in an inert atmosphere, damage tolerant, maintains its strength at high temperatures, and is resistant to thermal shock and chemical attack including high-temperature oxidation. Ti₃SiC₂ displays good oxidation resistance because of the presence of SiO₂.

Ti₃AlC₂ is another nanolaminated ternary compound that also exhibits superior metallic and ceramic properties [2]. However, Ti₃AlC₂ has been less well studied, owing to the fact that it is a relatively new member of the ternary carbides and because of the difficulties involved in preparing high purity, fully dense specimens [1]. The machinable, layered Ti₃AlC₂ is isostructural with Ti₃SiC₂. Ti₃SiC₂ and Ti₃AlC₂ form a complete range of solid solutions.

In this study, we used a powder mixture of TiC_x (x=0.6), Al and Si as the starting powders, and adopted a hot pressing method to synthesize highly pure, dense Ti₃(Al,Si)C₂ compounds. Our new process benefits from simultaneous reaction and densification at a relatively low processing temperature for a short reaction time. Changing the synthesizing process and the compound composition would be expected to affect the sample purity, sample density, and the sizes of the matrix grains, which could influence the oxidation kinetics and scale structures significantly.

The aim of this study is to describe the high temperature air-oxidation behavior of Ti₃(Al,Si)C₂ synthesized by our newly developed process. The characteristics of the oxides formed, the distribution and roles of Ti, Al, Si and C in the scale, and the oxidation mechanism are discussed based on the experimental results.

2. Experimental

Ti (< 45 m, 99.9 % purity) and C (~ 10 m, 99.95% purity)

powders were mixed at a molar ratio of Ti:C = 3:0.67, and pressed at 1500 °C for 3 h under a vacuum pressure of 1.3 Pa. The TiC_x (x=0.6) pellets synthesized were ground using a SPEX™ shaker mill, and sieved to <45m. Powders of TiC_x, Al (<45 m, 99.9 % purity), and Si (<70 m, 99.9 % purity) were mixed at a molar ratio of 3 : 0.75:0.25 in a SPEX™ shaker mill for 10 min, and hot pressed at 1400 °C under a pressure of 25 MPa for 60 min in flowing Ar gas. During the hot pressing, a reaction occurred between the TiC_x, Al and Si powders. The synthesized Ti₃(Al,Si)C₂ pellets were cut into specimens with dimensions of 1055 mm³, which were then ground to a 1000 grit finish, ultrasonically cleaned in acetone and methanol, and oxidized isothermally at 900 and 1000 °C in atmospheric air for up to 50 h. The weight changes were continuously monitored as a function of time using a thermogravimetric analyzer (TGA). The specimens were investigated by means of a differential thermal analyzer (DTA), an Auger electron spectroscope (AES), a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), an electronprobe microanalyzer (EPMA), and an X-ray diffractometer (XRD) with Cu-Kα radiation.

3. Results and discussion

Fig. 1 shows the SEM microstructure of the synthesized Ti₃(Al,Si)C₂. The fully compact specimen has lamellar grains about 10 μm in length and 4 μm in thickness.

Fig. 2 shows the XRD pattern of Ti₃(Al,Si)C₂, along with those of Ti₃AlC₂ and Ti₃SiC₂. These three compounds all have a layered hexagonal structure. Si atoms partially substituted into the Al sites in Ti₃AlC₂ to form Ti₃(Al,Si)C₂. Monolithic Ti₃(Al,Si)C₂ was successfully synthesized without any impurities. When changing from Ti₃AlC₂ to Ti₃(Al,Si)C₂, and then to Ti₃SiC₂, the diffraction angles such as those of the (006), (008), and (104) planes shifted to larger values, because the magnitude of the lattice parameter, c, decreased more significantly than that of a [3].

Fig. 3 shows the TG-DTA analytical results for Ti₃(Al,Si)C₂. The oxidation rate increased gradually with increasing oxidation temperature. From around 450 °C, the endothermic reaction due to the heating of the sample changed to an exothermic reaction, because Ti₃(Al,Si)C₂ began to be oxidized noticeably.

Fig. 4 shows the AES depth profiles of Ti₃(Al,Si)C₂ after oxidation at 900 °C for 7 min in air, which were obtained in order to understand the oxidation mechanism during the initial oxidation period. This inert Pt marker experiment was performed by sputter-depositing a thin Pt film on top of Ti₃(Al,Si)C₂ prior to its oxidation. From the location of the Pt film, it is seen that oxygen diffused inward, while Ti and Al

tended to diffuse outward. Carbon tended to escape from the surface, but Si simply stayed in the $Ti_3(Al,Si)C_2$ sample. It is noted that TiO_2 , being an n-type semiconductor, grows primarily by either the outward diffusion of interstitial Ti^{+4} ions or the inward diffusion of O^{2-} ions via oxygen vacancies, depending on the defect concentrations [4]. On the other hand, $\alpha-Al_2O_3$ is generally known to grow very slowly by the inward diffusion of oxygen [5].

4. Conclusion

Fully dense, monolithic $Ti_3(Al,Si)C_2$ compounds having lamellar grains were oxidized in air. $Ti_3(Al,Si)C_2$ oxidized nearly parabolically at 900 and 1000 °C according to the eq.; $Ti_3(Al,Si)C_2 + O_2 \rightarrow$ rutile- $TiO_2 + \alpha-Al_2O_3 +$ amorphous $SiO_2 + (CO \text{ or } CO_2)$.

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6 References

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