OXIDATION of $Ti_{n+1}AlX_n$ where n = 1-3 and X is C and/or N

By

M. W. Barsoum, N. Tzenov, A. Procopio, T. El-Raghy and M. Ali
Department of Materials Engineering, Drexel University,
Philadelphia, PA 19104

Abstract

In this, paper we report on the oxidation kinetics in air of the ternary compounds: Ti_2AlC, $Ti_2AlC_{0.5}N_{0.5}$, $Ti_4AlN_{2.9}$ and Ti_3AlC_2. For the first two, in the 1000-1100 °C temperature range and for short times (≈ 20 hrs.), the oxidation kinetics are parabolic. The parabolic rate constants are, k_x (m^2/s) = 2.68x10^5 exp –491.5 (kJ/mole)/RT for Ti_2AlC, and 2.55 x10^5 exp – 458.7 (kJ/mole)//RT for $Ti_2AlC_{0.5}N_{0.5}$. At 900 °C the kinetics are quasi-linear, and up to 100 hrs. the outermost layers that form are almost pure rutile, dense and protective. For the second pair, at short times (< 10 hrs.) the oxidation kinetics are parabolic at all temperatures examined (800-1100°C), but become linear at longer times. The k_x values are 3.2x10^5 exp – 429 (kJ/mole)/RT, for $Ti_4AlN_{2.9}$ and 1.15x10^5 exp – 443 (kJ/mole)//RT for Ti_3AlC_2. In all cases, the scales that form are comprised mainly of a rutile-based solid solution, $(Ti_{1-y}Al_y)O_{2-y/2}$, where $y < 0.01$, and some Al_2O_3. The oxidation occurs by the inward diffusion of oxygen and the outward diffusion of Al and Ti. The C and N atoms are presumed to also diffuse outward through the oxide layer. A generalized model is presented, the basic premises of which are that the subjection of the $(Ti_{1-y}Al_y)O_{2-y/2}$ solid solution to an oxygen potential gradient results in its demixing, with the Al^{3+} ions dissolving into the rutile at the low oxygen partial pressure and their precipitation as Al_2O_3 at the high partial pressure side. It is this demixing that is believed to result in the formation of pores that concentrate along planes, especially at longer times and higher temperatures. These layers of porosity impede the diffusion of Al, but not those of Ti and oxygen, which results in the formation of a highly striated scales where 3 layers: an-Al_2O_3-rich, a TiO_2-rich and a porous layer repeat multiple (> 10) times (Fig. 1). Comparison with previously published results on the oxidation of Ti_3SiC_2 leaves little doubt that dissolution of the Al in the reaction layer enhances the oxidation kinetics. This is most probably accomplished by an increase in the oxygen vacancy concentration. The ramifications of this model to the oxidation of Ti-aluminides will be discussed.

Figure 1: Cross-sectional SEM micrographs of a Ti_3AlC_2 sample oxidized in air at 1100°C for 64 h. Three layers, a bright TiO_2 layer, a darker alumina rich layer, and planes of porosities repeat as a result of demixing. The oxide/air interface is located at the top of the micrograph.