The fluorine effect for the high temperature oxidation protection of Ti-based alloys – A thermodynamic approach

A. Donchev, M. Galetz

DECHEMA-Forschungsinstitut, Theodor-Heuss-Allee 25, 60486 Frankfurt/Main

Titanium based alloys and intermetallics belong to lightweight materials. The replacement of the heavy Ni-based materials used today in conventional high temperature applications by these groups of materials would increase the efficiency of such new engines. However, titanium forms a fast growing oxide scales (TiO_2) during high temperature exposure in oxidizing environments which is non-protective. Intermetallic titanium aluminides form mixed oxide scale (TiO_2/Al_2O_3) which also shows no protective effect. Therefore, the improvement of the high temperature oxidation resistance is a prerequisite before any use of such alloys at elevated temperatures.

The oxidation resistance of TiAl alloys can be drastically increased by doping the surface zone with small amounts of halogens. The oxidation mechanism changes from mixed oxide scale formation to protective alumina formation (Al_2O_3).

This change in the oxidation mechanism is caused by the almost exclusive formation of gaseous aluminum halides during the incubation period of the high temperature exposure. Within a certain range of the halogen concentration the partial pressures of aluminum halides exceed those of the titanium halides by several orders of magnitude. FactSage calculations using the equilibrium menu and varying the halogen partial pressure within the relevant temperature range from 700 °C – 1100°C have shown that $AlX_{(g)}$ (X = F, Cl, Br or I) is the most volatile compound. This species is oxidized towards aluminum oxide during its outward diffusion through the naturally grown oxide. Hence, a protective alumina layer is formed. The enthalpies of formation for the reactions of the different halides were calculated and the results were compared. The reactions with fluorine possess the highest enthalpy within the group of halogens and the reactions of aluminum are also favorable compared to those of titanium.

For conventional titanium alloys the aluminum content is not high enough to get the halogen effect to operate. Therefore, aluminum enrichment in a narrow surface zone has to be achieved before any halogen treatment can be applied. These treatments were also successful, so that the halogen effect was transferred to alloys with much lower aluminum content. The use of such lightweight materials in several high temperature applications becomes possible by such treatments.