Influence of humidity on the high-temperature oxidation of Si_3N_4-TiN composites

A.Feldhoff, M.-F.Trichet, L.Mazerolles, M.Backhaus-Ricoult

Centre d'Etudes de Chimie Métallurgique, CNRS, UPR2801, 15 rue George Urbain, F-94407 Vitry sur Seine, France, Phone: +33-1-56-70-30-31, Fax: +33-1-46-75-04-33, feldhoff@glvt-cnrs.fr

The oxidation in air of Si_3N_4-based ceramics containing 35vol% of TiN second phase particles and different additive contents (Fig. 1) has been studied in a wide range of temperature as a function the humidity level in the environment. Oxidized samples were characterized by X-ray diffraction, scanning and transmission electron microscopy.

In the first stages of oxidation, at around 600-800ºC, only TiN particles at the outer surface are locally oxidized to nanocrystalline rutile. With increasing temperature, lateral growth of rutile occurs on the surface and eventually yields a dense surface scale. During oxidation at 1000°C, a multilayered scale develops (Fig. 2). Its top layer is made of polycristalline rutile (TiO_2). Beneath, an irregular glass layer with many dispersed nanocrystallites is observed (Fig. 3, Fig. 4). Next to that layer, a subscale is found, in which the silicon nitride matrix is preserved, but rutile and a large number of small and large size pores are found instead of the TiN particles. In this latter subscale, important modifications in distribution and composition of the intergranular glass are found. These observations show that at 1000°C considerable matter transport takes places within the intergranular glass and controls the oxidation behaviour. In this temperature range, oxidation mechanism and kinetics are strongly affected by humidity in the environment: In first stages of lateral growth of the rutile top layer oxidation is slowed down by the presence of water. In later stages the TiO_2 top layer is thicker under humid than under dry air. Anyhow, the integral scale thickness is similar. We think that water is dissolved in the glass, thereby strongly modifying its network structure and its transport properties.

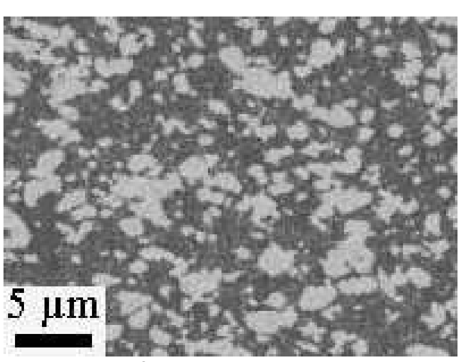

Fig. 1: BSE image of an as-sintered composite (light grey: TiN, dark: Si_3N_4).

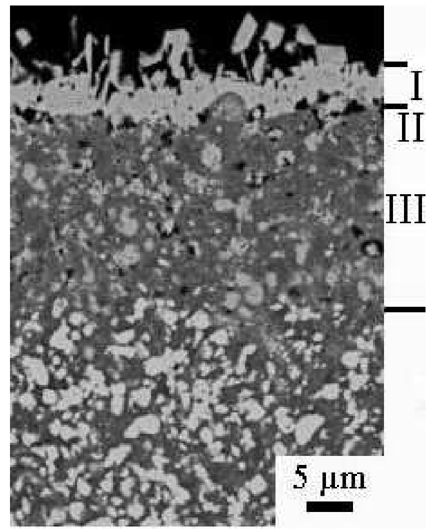

Fig. 2: BSE image of a multilayered oxidation scale, developped at 1000°C after 24 hours in dry air.

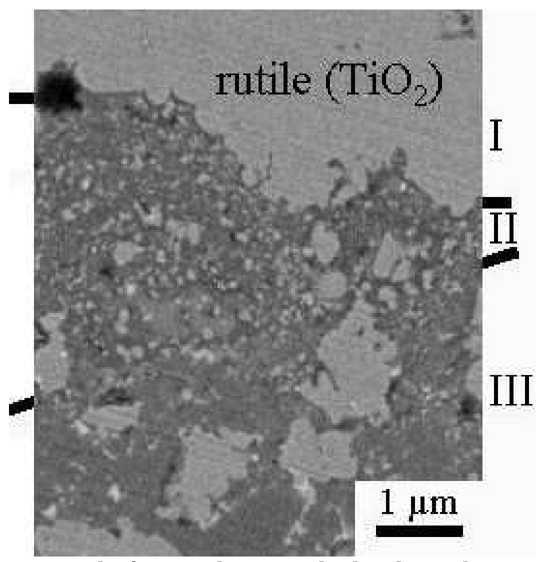

Fig. 3: Detail of an oxidation scale developped at 1000°C after 24 hours in humid air. Note rounded surfaces of rutile grains of top layer (I) in contact with glass layer (II).

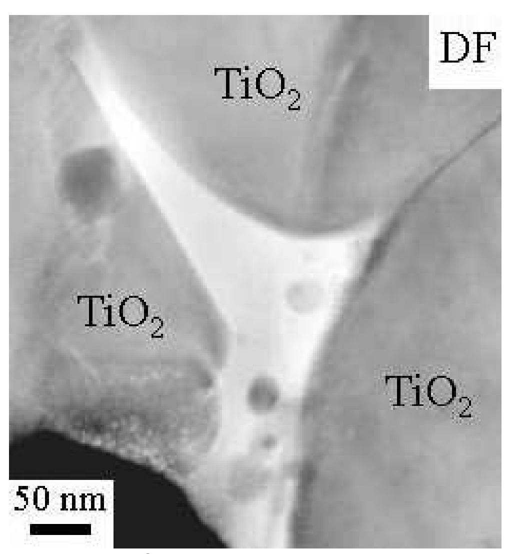

Fig. 4: TEM dark-field revealing nanoprecipitates in glass between rutile grains in top layer of oxidation scale.