

Basic B₄C oxidation tests in the thermal balance with respect to reaction kinetics under severe accident conditions

W. Krauss, G. Schanz, H. Steiner

Abstract:

Separate effect tests are being performed on the oxidation of pure B₄C with respect to degradation of control rod segments using a thermal analysing system (TG and DTA). This type of investigation is part of a common materials testing program at FZK executed with different test facilities, which are ranging from small specimen tests over medium sized control rod segment tests to large scale bundle tests. The whole work is integrated in the EC-COLOSS program and should provide an understanding of mechanisms occurring during B₄C oxidation under various environmental conditions including the formation of methane.

Using the thermal balance device the B₄C reactions are studied in detail under various well defined conditions including non-prototypical ones. The strategy of these studies is to contribute to the identification of those individual mechanisms of the reaction behaviour sequence which determine reaction path, products, as well as reaction rate. The experimental work is supported by modelling activities to guarantee a correct separation of counteracting mechanisms and reaction paths and to deliver data on reaction kinetics to code developers for use in risk assessment or in severe accident management.

Up to now measurements were performed on B₄C, B₂O₃ and C with respect to humidity desorption, net mass change during oxidation and evaporation of carbon and boron compounds. The test atmospheres were argon, argon/oxygen (80/20) and argon/steam.

Dense B₄C oxidises at low temperatures in Ar/O₂ atmosphere with a weight gain corresponding to the chemical reaction $B_4C + 4O_2 \rightarrow 2B_2O_3 \text{ (solid)} + CO_2 \text{ (gas)}$ and formation of protective layers which lead to parabolic reaction kinetics. At temperatures higher than 800°C evaporation of B₂O₃ significantly increases and makes the TG evaluation more complex. At very high temperatures (T > 1200 °C) evaporation seems to be dominant. Similar behaviour is indicated for reactions in Ar/steam mixtures however with different time dependence.

It was found that B₄C samples show during the beginning of the oxidation reaction (short test times) a resulting mass increase whereas for long test durations a mass decrease is detected. The time scale for crossing the maximum depends at least on test temperature and atmosphere composition.

With the performed modelling the mass change behaviour of transiently heated B₄C samples in dry Ar/O₂ atmosphere under isothermal conditions for several hours at low temperatures could be simulated. Work is in progress to describe the high temperature behaviour and is able at the moment to explain the maximum in the TG mass signal by combining two counteracting mechanisms, the formation of an oxide barrier and the evaporation of the formed scale. This is seen as a first step in interpretation of B₄C SETs and has to be extended to tests performed with the other used facilities. At the moment it is clear that the results obtained from B₄C tests are more complex in interpretation than expected, but the modelling efforts have already shown the potential of the experimental data.