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Effects of B4C control rod degradation under severe accident

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1. Introduction

Boron carbide (B_4C) is widely used as absorber material in western boiling water reactor (BWR), some PWR, EPR and Russian RBMK and VVERs. B_4C oxidation is one of the important phenomena of in-vessel. Reasons of the importance of B_4C oxidation is as follow.

- B_4C oxidation causes earlier absorber melting by eutectic [1-3] than fuel assembly melting. It is not clearly revealed what impacts of released absorber melt exist on the fuel assembly.
- B_4C oxidation is highly exothermic and produce more than 6~7 times of the amount of hydrogen than the steam oxidation of the same mass of Zircaloy.
- Gaseous species containing carbon and boron are formed which may affect the fission product chemistry during transport in the containment (e.g. for the release of organic iodine compounds).

Many experiments about B_4C oxidation have been conducted since 1960s. Early experiments had been performed at below 1000°C [4-7]. Other experiments about oxidation of hot-pressed B_4C pellets had been implemented at rather higher temperature (up to 1300°C) than previous works by Sato et al. [8]. However, temperatures of interest for severe accident about B_4C oxidation are above 1300°C when failure of the control rod clad (stainless steel) and of the guide tube (Zircaloy) are occurred. Therefore, an experiment of B_4C oxidation and a subsequent degradation about high temperature (up to 1600°C) as a SET (Separate-Effects Test) was launched at FZK within the EC COLOSS project in the frame of the 5th Framework Program [9]. Also some experimental programs as an IET (Integral-Effects Test) such as QUENCH-07 [10], QUENCH-09 [11], and the French PHEBUS FPT-3 [12] were performed.

In the present paper, the main results and knowledge gained regarding the B_4C control rod degradation from above mentioned experiments are reviewed and arranged to inform its significance on the severe accident consequences.

2. B_4C control rod degradation mechanism

First of all, coolant temperature increases once the severe accident initiated. Also core is exposed to steam conditions by the evaporated coolant in reactor vessel. Then oxidations of fuel rods, core baffle or shroud, core support barrel, and control rods are followed. In this study, B_4C control rod oxidation and degradation is reviewed.

2.1 B_4C control rod degradation by oxidation

The following chemical reactions between B_4C and steam based on [13] are considered to play a role during the oxidation of B_4C.

$$B_4C + 7H_2O \rightarrow 2B_2O_3 + CO + 7H_2 - 760$$
$$B_4C + 8H_2O \rightarrow 2B_2O_3 + CO_2 + 8H_2 - 792$$
$$B_4C + 6H_2O \rightarrow 2B_2O_3 + CH_4 + 4H_2 - 987$$

The last numbers of right hand side are enthalpy changes in kJ per mol of the leftmost specie. They do not include enthalpy changes due to the B_2O_3 evaporation. Extra steam reacts with B_2O_3 (liquid boron oxide) to form volatile boric acid:

$$B_2O_3 + H_2O \rightarrow 2HBO_2$$
$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$$

In addition, oxidation of Zr, which is included in the guide tube of control rod, is considered as follow:

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 - 595$$

According to the above chemical reactions, guide tube of B_4C control rod is oxidized firstly under the severe accident condition. There are no significant damages although pure B_4C control rod is exposed to steam flow. Only the oxide scale (ZrO_2) is formed on external surface of guide tube. Local interactions of stainless steel (SS), B_4C, and Zircaloy may be occurred during the forming oxide scale. Eutectic melt is formed between B_4C and oxide scale at temperatures above 1250°C in the system of B_4C-SS and SS-Zircaloy. From this moment, enhanced degradation of B_4C control rod begins. The rapid oxidation of B_4C and absorber melt is occurred after the failure of the oxide scale at high temperatures of about 1500°C.

Important thing is that these absorber melts are relocated into the fuel rods at much less temperature than fuel rod melting temperature as depicted in Fig. 1.

The relocated absorber melts will interact chemically with fuel rod [14]. Also this chemical interaction between absorber melts and fuel rod may contribute overall fuel assembly degradation or damage because the absorber melts are very corrosive towards the ZrO_2 crucibles under oxidizing conditions. So the control rod failure in a fuel assembly may cause the early failure of surrounding fuel rods connected with release of fission products and relocation of UO_2 containing melts. Unfortunately, we have not known exactly up to now how much damage are exerted onto the fuel assembly by the released absorber melt. Therefore, computational analysis of severe accident with respect to core degradation cannot be substantialized precisely because of uncertainty about liquid absorber melt relocation in fuel assembly [15].

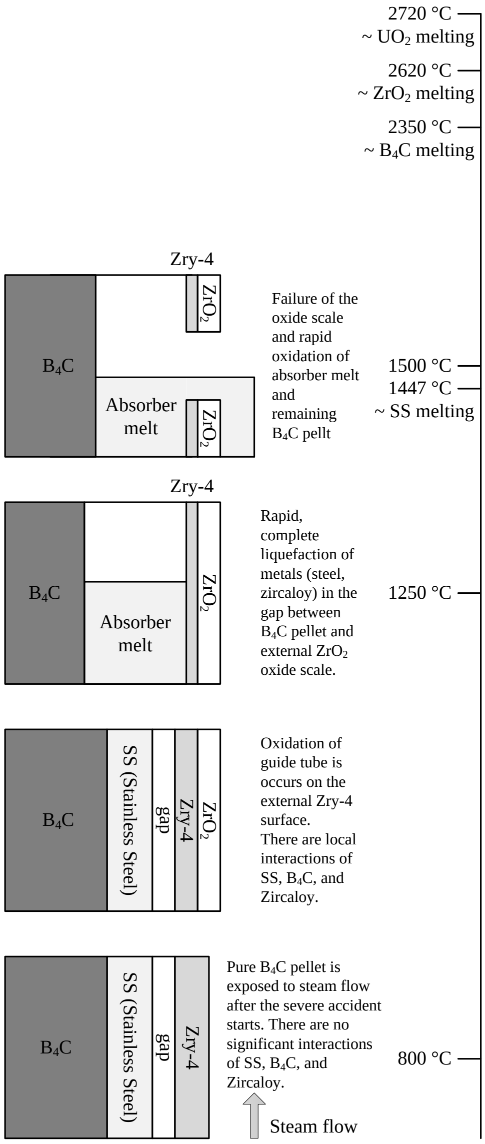

Fig. 1. Schematic Diagram of B_4C control rod degradation during severe accident

2.2 Hydrogen production, chemical heat release, and organic iodine

In addition, the quantitative contribution of B_4C oxidation to hydrogen production was yielded from mass spectrometer data for CO, CO_2, CH_4, and H_2 in QUENCH-07 and QUENCH-09 experiment [14]. This contribution is limited to generally less than 10% for hydrogen generation rate, total hydrogen production, as well as total chemical energy release. This is relatively large amount because B_4C control rod has only a few percent of mass in comparison with UO_2 fuel rod in core. It makes the control rod oxidation important in-vessel phenomenon in severe accident.

The main gaseous reaction products of B_4C oxidation are CO and CO_2. Only a small amount of CH_4 is released at relatively low temperature of 800°C. The CH_4 release rate decreases to almost zero above 1000°C [9].

The oxidation of degradation products of the control rod may also have indirect impacts on hydrogen production. In any case, it increases temperature locally and hence it may promote the zirconium oxidation. Such indirect contributions on hydrogen production were assessed by comparing with QUEUNCH-07 and QUENCH-08. It was concluded in [14] that the indirect influence of control rod oxidation on zirconium oxidation must be rather limited to some extent. In contrast to this experimental conclusion, calculations for these two tests with ICARE/CATHARE suggest [16] that indirect contributions to hydrogen production exceed direct ones appreciably, but calculated temperatures, especially for the benchmark of QUENCH-07, are so far overestimated that such a conclusion is not reliable.

3. Summary

Main B_4C degradation consequences on the fuel assembly are listed as follow:

- Absorber melts are formed by eutectic at lower temperature than its melting temperature in early phase of severe accident.
- The absorber melts are relocated between B_4C and oxide scale. This low-viscosity melts are not oxidized because they are protected from steam by forming a dense oxide scale (ZrO_2).
- Oxidation of absorber melts is rapidly occurred shortly after failure of the oxide scale. It results in hydrogen generation.
- Failure of the oxide scale of control rod causes surrounding fuel rod degradation. Pseudo-ternary SS/B_4C/Zr melts attacks to oxide scale of fuel rod. It may result in release of UO_2 fuel or fission products.

- Contribution of the oxidation of B_4C to the hydrogen production rates and total chemical heat release are limited below 10%, respectively.
- According to the QUENCH-07 experiment results, lateral and axial distributions of released absorber melt are the form of melt lump and falling droplet, respectively, if oxide scale failure is occurred shortly after the forming absorber melt.
- The droplets are not oxidized. However, mobility of the lump is limited by continuing oxidation. Also the lump interacts chemically with surrounding fuel rod.
- According to the QUENCH-09 experiment results, guide tube is superheated and viscosity of absorber melt within control rod is decreased if oxide scale continuously maintains its integrity.
- Indirect impact of B_4C control rod degradation on the hydrogen production is believed up to now that it lead not to the considerable contribution of the hydrogen generation, and its amount is limited.

4. Conclusion

In this paper, the role of B_4C control rod oxidation and the subsequent degradation on the severe accident consequences is reviewed with available literature and report of previous experimental program regarding the B_4C oxidation. From this review, it seems that the contribution of this B_4C oxidation on the accident progression to the further severe accident situation is not negligible. For the future work, the extensive experimental data interpretation will be performed to assess quantitatively the effect of B_4C oxidation and degradation on the various postulated severe accident conditions.

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