MATERIAL OPERATING BEHAVIOUR OF ABB BWR CONTROL RODS

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Abstract

The BWR control rods made by ABB use boron carbide (B4C) and hafnium as absorber material within a cladding of stainless steel. The general behaviour under operation has proven to be very good. ABB and many of their control rod customers have performed extensive inspection programs of control rod behaviour. However, due to changes in the material properties under fast and thermal neutron irradiation defects may occur in the control rods at high neutron fluences. Examinations of irradiated control rod materials have been performed in hot cell laboratories. The examinations have revealed the defect mechanism Irradiation Assisted Stress Corrosion Cracking (IASCC) to appear in the stainless steel cladding. For IASCC to occur three factors have to act simultaneously. Stress, material sensitization and an oxidising environment. Stress may be obtained from boron carbide swelling due to irradiation. Stainless steel may be sensitized to intergranular stress corrosion cracking under irradiation. Normally the reactor environment in a BWR is oxidising. The presentation focuses on findings from hot cell laboratory work on irradiated ABB BWR control rods and studies of irradiated control rod materials in the hot cells at PSI. Apart from physical, mechanical and microstructural examinations, isotope analyses were performed to describe the local isotopic burnup of boron. Consequences (such as possible B4C wash-out) of a under operation in a ABB BWR, after the occurrence of a crack is discussed based on neutron radiographic examinations of control rods operated with cracks.

1. INTRODUCTION

ABB Atom has delivered almost 4000 control rods to Boiling Water Reactors (BWRs) around the world. More than 1000 of these rods have been inspected after varying time of operation and at varying levels of neutron exposure. Besides the visual pool-side inspections, control rod wings with cracks have been analysed by neutron radiography to reveal the behaviour of irradiated boron carbide behaviour in case of cracking and water intrusion. Irradiated control rods and irradiated control rod material samples have been examined in hot cell laboratories to understand the materials behaviour and properties due to fast and thermal neutron irradiation.

2. ABB BWR CONTROL ROD DESIGN

The basic design of ABB BWR control rods is shown in Figure 1. Four stainless steel plates are forming a cruciform shaped rod. The steel quality initially used from start was AISI 304L SS which has in later manufacturing been replaced by AISI 316L SS. Boron carbide (B_4C) powder with a void volume of 30% is used as absorber material together with hafnium.

3. NEUTRON IRRADIATION OF CONTROL ROD MATERIALS

Neutron irradiation is known to the change properties of the materials used in control rods. Some of these changes have an influence on the control rod behaviour.

3.1. Stainless steel

Neutrons of energies above 1 MeV cause hardening, increase in yield and ultimate strength, segregation etc. in the stainless steels used. Segregation of chromium from the grain boundaries of the steel means that the material becomes sensitized for stress corrosion attack in the grain boundaries. The impact, for the operational behaviour, of other changes in the stainless steel material structure and properties is under investigation since not yet fully understood.

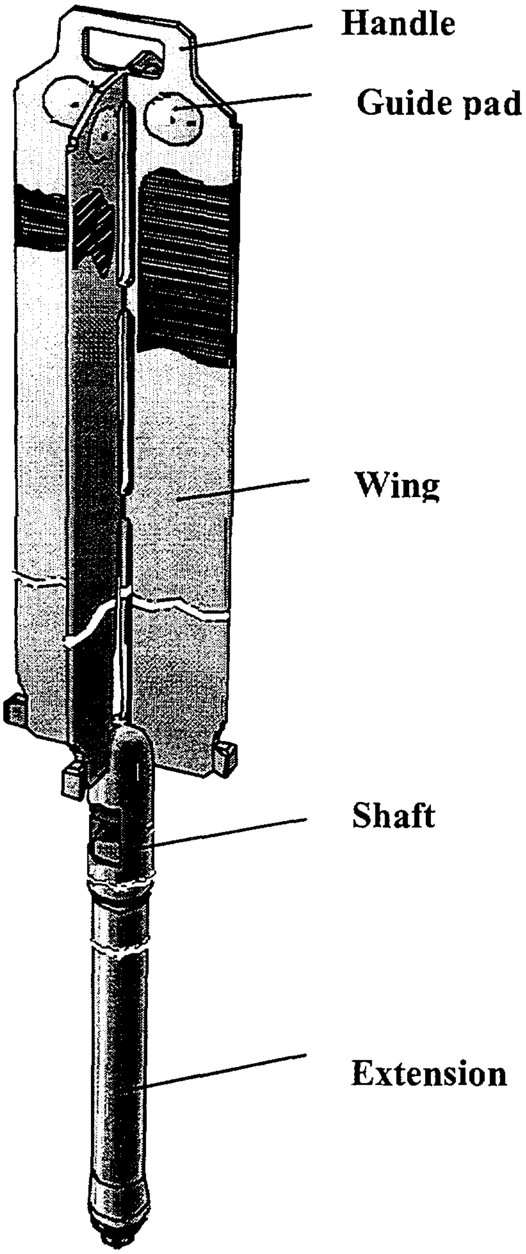

FIG. 1. Basic design of the ABB BWR control rod

The environmental assisted cracking occuring in control rods is intergranular and called Irradiation Assisted Stress Corrosion Cracking (IASCC). IASCC needs three simultaneous factors to occur:

1. Stresses - in a control rod, these can be caused by the swelling boron carbide;
2. Material sensitization - chromium depletion in grain boundaries is such a factor caused by neutron irradiation, there might be others not yet understood;
3. Oxidising environment - IASCC due to chromium depletion in the grain boundaries requires an oxidising environment. There seems, however, to be other factors at higher irradiation eliminating the requirement of oxidising conditions.

The crack mode has been observed in several investigations and the picture in Figure 2 is from a Post Irradiation Examination (PIE) of a ABB BWR control rod at the Paul Scherrer Institute (PSI). The material is Type 304L stainless steel. In Figure 3, a grain boundary STEM analysis (made by Magnox Electric) of element profiles, from the same material shows the depletion of chromium from the grain boundary. The neutron fluence was $3 \cdot 10^{21}$ n/cm^2 (E>1MeV).

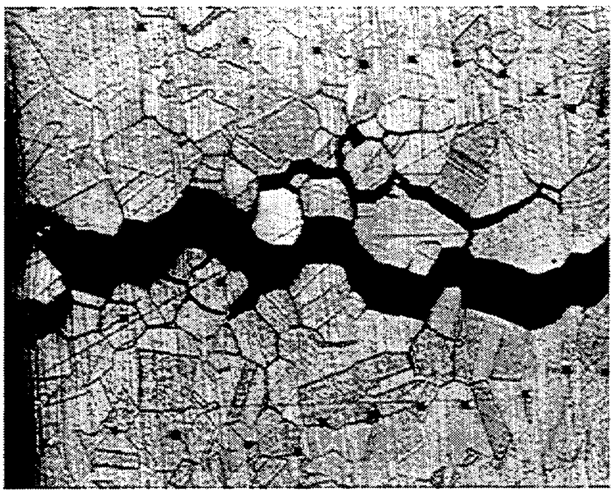

FIG. 2. Intergranular crack mode in irradiated type 304L SS, 3 · 10^{21} n/cm^2 (E>1MeV)

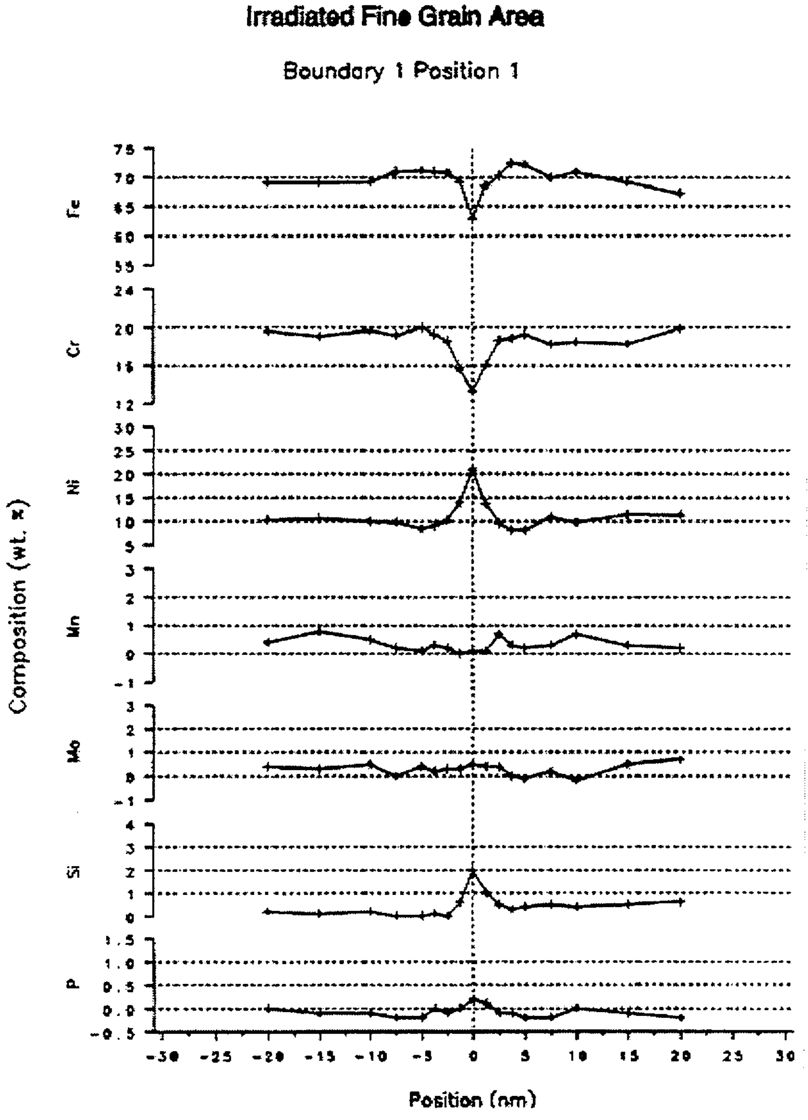

FIG. 3. Concentration profiles of elements in type 304L SS. irradiated to 3 · 10^{21} n/cm^2 (E>1MeV)

Figure 4 shows the chromium profile of the material before irradiation. In this non-irradiated condition there is an enrichment of chromium to the grain boundary. The material was in a solution heat treated condition prior to irradiation.

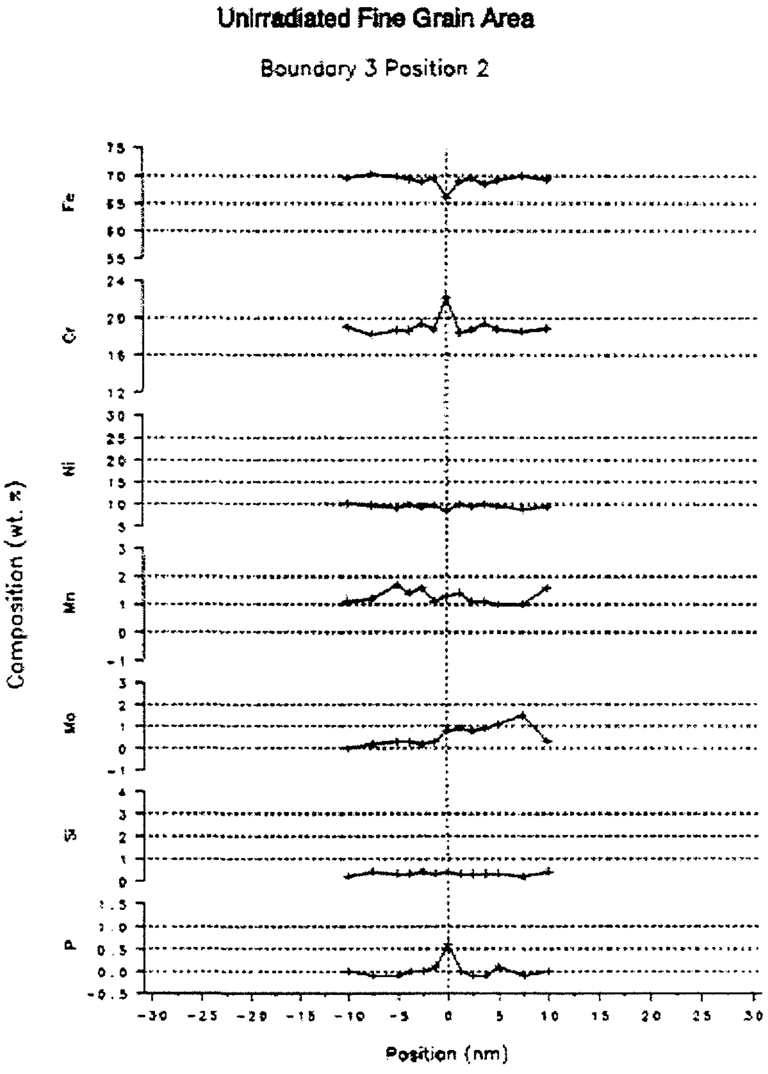

FIG. 4. Concentration profiles of elements in non-irradiated type 304L SS

Studies by Ljungberg and Jenssen [1] have shown that Type 316L SS material is less susceptible to IASCC after irradiation to relevant BWR neutron exposure levels, $10^{21} - 10^{22}$ n/cm^2 (E>1MeV), see Figure 5.

Control rod experiences with this material show a significant delay in IASCC susceptibility for Type 316L SS compared to Type 304L SS. However, immunity against IASCC seems to be best obtained by avoiding high stresses in the steel.

3.2. Boron Carbide (B_4C)

By absorption of thermal neutrons, the ^{10}B isotope in the B_4C gets transmuted to helium and lithium according to the reaction:

$^{10}B + n \rightarrow {}^{7}Li + {}^{4}He + 2{,}8$ MeV

This means that B_4C is swelling due to neutron irradiation since most of the helium atoms formed by the neutron absorption reaction are trapped in the boron carbide crystals.

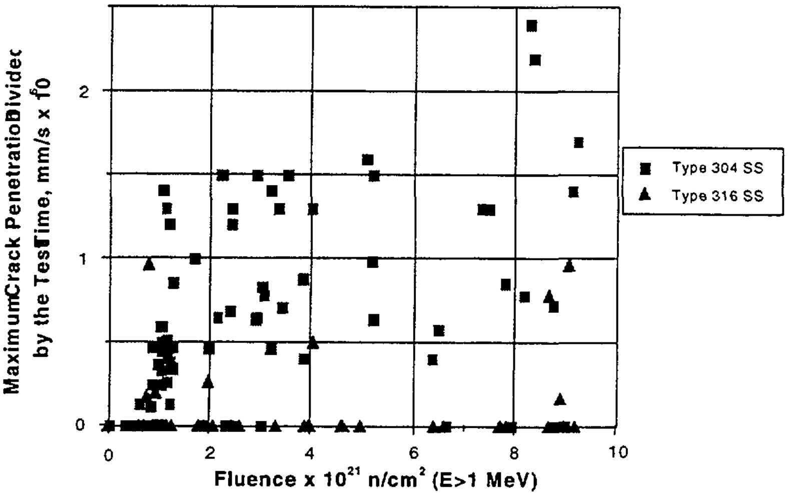

FIG. 5. Comparison of susceptibility to IASCC of type 316L SS and type 304L SS

Secondly the chemical properties may be changed when the B_4C structure is disturbed by formation of Li and He in the crystals, replacing some boron atoms. Smaller amounts of tritium (^3H) are also formed during irradiation by other, less frequent transmutation reactions. This has no impact on the control rod behaviour but it can be used to monitor the status of the control rod inventory in the reactor core, as discussed later in this paper.

Swelling of the boron carbide as well as the helium gas release are important parameters when designing the control rod. Experiences from control rod operation has shown that swelling has been the service lifetime determining parameter but not the helium release. A hot cell examination of boron carbide samples, irradiated under relevant conditions in the Forsmark 1 BWR, has been performed at PSI [2]. The study showed that the fraction released helium from the irradiated boron carbide was much lower than the helium release curve presented in [3].

3.3. Hafnium

Hafnium in BWR control rods is used in locations with high local neutron exposure. Hafnium is heavy and expensive which explains the limited use of the material in the rods. The benefit of using hafnium is the absence of swelling during irradiation. This behaviour has been verified by a PIE on an irradiated ABB BWR control rod with hafnium tip at PSI, [4]. The same study revealed that that hydrogen content of hafnium in a BWR control rod is low even after operation, as long as the control rod is free from cracking. This result is in agreement with calculations made by ABB [5]. Thus it is shown, that the hydrogen concentration in the BWR environment, also in case of hydrogen water chemistry operation, is too low to cause significant concentration of hydrogen within the control rod although the stainless steel cladding has high permeability for hydrogen. Tritium formed in the boron carbide during irradiation is retained in the boron carbide structure [3] and does not influence the hafnium. The latter has also been proven by inspection of hundreds of intact control rods with hafnium, showing no swelling.

If a crack occurs that leads to water intrusion hydrogen may be formed by corrosion reactions as well as by reaction between lithium and water. In such cases hydriding of hafnium has been experienced as shown in Figures 6 and 7. Experiences by use of hafnium in ABB BWR control rods show that no significant hydrogen concentrations are obtained in the hafnium of an intact control rod. Water intrusion after rod cracking is hence the only possible source to hafnium hydride formation.

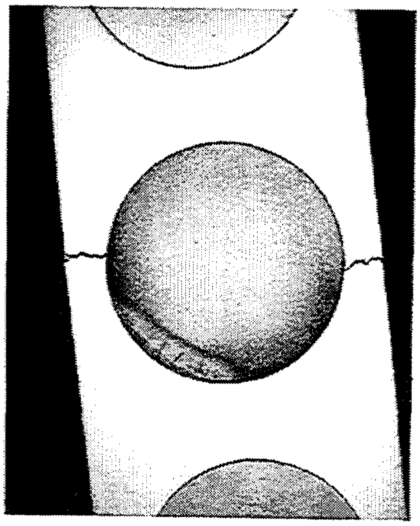

FIG. 6. Hafnium plug with hydride formation

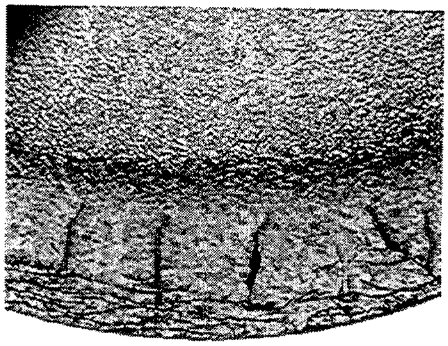

FIG. 7. Magnification of hafnium hydrides

4. CONTROL ROD MANAGEMENT

Guidelines for control rod management must be based on experience data from inspections and PIEs. More than thousand control rods of ABB BWR design have been inspected after irradiation. Many have also been subject for PIEs such as neutron radiography and hot cell examinations. Guidelines are formulated for each different design by frequent inspections of leading rods of that particular design. By inspections, the general appearance of the rod after operation as well as possible crack appearance is observed.

4.1. Neutron radiography

In the case of water intrusion into a control rod, by crack occurrence, the consequences for the boron carbide absorber material is of vital importance. For this reason an extensive work by neutron radiography has been performed especially in Swedish BWRs. Control rods from shut-down operation and control cell operation, with cracks, have been analysed in this way, see Table I.

TABLE I. RESULTS OF NEUTRON RADIOGRAPHY

Reactor	Type	Year	No of Wings	Estimated Tip* exposure (snvt)	B_4C Leach-out
A	CR70	1985	2	6,6 – 7,1	No
A	CR70	1986	2	6,8 – 7,3	No
B	CR70	1986	13	6,8 – 7,7	limited loss in 2 blades
C	CR70	1986	10	7,6 – 7,7	limited loss in 4 blades
B	CR70	1987	13	7,2 – 8,1	limited loss in 2 blades
B	CR85	1991	1	5,0	limited loss in 1 blade
D	CR85	1992	2	4,4**	limited loss in 2 blades
E	CR82	1993	1	4,8	limited loss in 1 blade

* Tip means the uppermost absorber hole

** Top quarter exposure

By exposing a control rod wing to a neutron source and detecting the non-absorbed neutrons a clear picture of the boron carbide content can be obtained. An example of such a picture is shown in Figure 8. The lighter areas in the upper absorber bores reveal some B_4C loss.

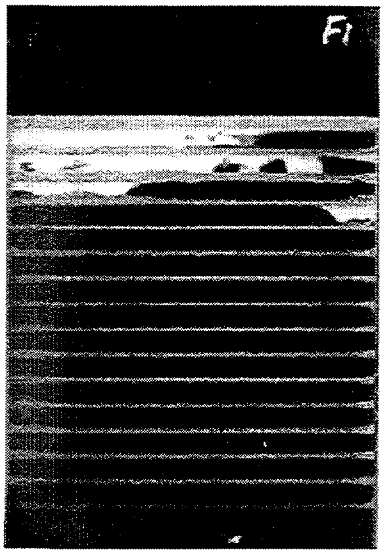

FIG. 8. Neutron Radiography picture of an ABB BWR control rod wing tip

In the cases where losses of B_4C has been detected it has been very limited, which means that there has been no influence on the shut-down margin. The conclusions from these studies are that a control rod can be operated with cracks that appear during a operating cycle. The recommendation of ABB is nevertheless not to start up a reactor with known cracks in the rod wings.

4.2. Tritium

Tritium (^3H) is produced in the B_4C absorber by several reactions with fast and thermal neutrons. Other sources for tritium production are:

- neutron activation of deuterium in the reactor water;
- neutron activation of lithium contamination in the reactor water;
- ternary fission of the fuel.

The reactor water content of tritium will reach a stable level during operation. The level is determined by the tritium production in the reactor water and the reactor water exchange under normal conditions. It has been shown that a control rod with cracks may contribute to the tritium content of the reactor water in case of water intrusion. This intrusion leads to formation of THO. The tritiated water may then be mixed with the reactor water. For a plant where the basic tritium level under normal operating conditions is known, increased tritium levels probably indicate control rods with cracking. This means that the planning of control rod inspections can be made more efficient by following the tritium content in the reactor water. A method for using tritium analysis in the control rod management work is now under development by ABB.

5. DEVELOPMENT

Experiences from operation of ABB BWR control rods has led to the conclusion that avoiding stresses in the stainless steel clad material is the best way to extend the mechanical service life time of control rods.

Normally boron carbide is used as a powder within a stainless steel cladding. To avoid stresses in the steel from swelling boron carbide, the void volume of the powder must accommodate the increasing volume of the grains. If we assume that this would be the case we receive a decreasing void in boron carbide powder with irradiation. Our experiences indicate that a large variation prevails between control rods regarding the behaviour of the powder. Modelling the behaviour of the swelling powder is hence a difficult task.

By using boron carbide without internal void, several advantages are obtained:

- The behaviour of a theoretical dense body is much easier to model;
- By allocating the void outside the dense body, the use of the void for accommodation of swelling is ensured;
- Designing a control rod to avoid stresses is more readily done.

A concept to use almost theoretically (>99%) dense boron carbide pins instead of powder has been developed by ABB. The concept, that includes boron carbide compositions in the range of B_4C to $B_{8.5}C$, has been studied by irradiation of pins in the Forsmark 1 BWR and a PIE of the pins at PSI. From this study swelling has been determined as a function of ^{10}B depletion in the pins. The accuracy in the modelling of the swelling behaviour of the pin can be improved by determining the ^{10}B depletion profile through the body. Such a work was performed at PSI by using the SIMS technique.

5.1. Isotopic analysis of a theoretically dense boron carbide pins with SIMS technique

Due to the large thermal neutron capture cross section of ^{10}B, its burnup and helium production within a boron carbide absorber body is inhomogeneous. The developed SIMS technique now offers a direct measure of the radial burnup of ^{10}B in a $B_{8.5}C$ neutron absorber test sample with almost theoretical density. The sample, previously mounted like a ceramographic specimen is bombarded within an ultra-high vacuum chamber with a focused ^{133}Cs primary ion beam and the secondary ions emitted from the sample surface are detected and separated according to their ion mass. The technique allows to measure quantitatively the radial boron burnup.

5.1.1. Experimental

The test sample selected for radial boron burnup analysis was a cylindrical $B_{8.5}C$ sample of 1.75 mm diameter and (initially) natural isotopic content, brought to an estimated burnup of 55 %. The sample was mounted in araldite, (wet) ground with diamond discs (125, 40, 20 and 10 μm) and polished with 3 μm diamond paste, see Figure 9. The formation of cracks at the specimen periphery is clearly visible.

After an ultrasonic cleaning in alcohol, the sample was introduced into an ATOMICA-4000 SIMS and sputtered with a ^{133}Cs primary ion beam of $\cong$ 30 μm diameter at 11 kV energy and 120 nA current. For each analysis a shallow 50x50 μm^2 crater was eroded away from the sample surface before performing the isotopic measurements in order to get stable secondary ion count rates. The secondary ion optics was (individually) tuned for ^3H, ^7Li ^{10}B and ^{11}B analysis (the tuning was set the same for the latter two nuclides).

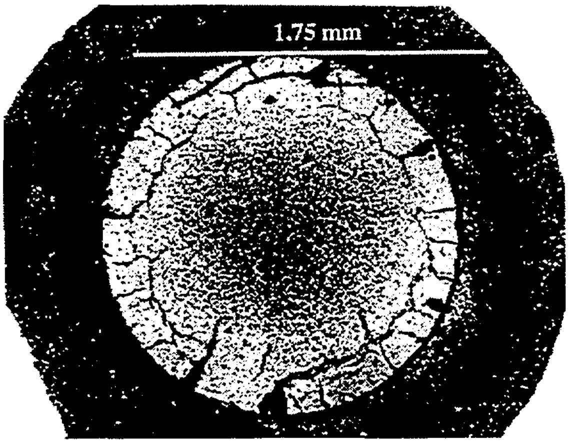

FIG. 9. Macrography of the hipped, irradiated $B_{8.5}C$ specimen after preparation

A "checker board" area scan of 50 by 50 measurement points was then performed across the sample surface with steps of 50 µm. A direct (non-corrected non-normalized) area scan of the ^{10}B and ^{11}B count rates is presented in Figure 10. This direct information had to be corrected because of problems with the sample holder movement (which simulates an oval sample shape) and normalized (presently with ^{11}B) because a direct individual secondary ion count rate conversion to an isotopic surface concentration requires a careful calibrations. The isotopic distribution of the two boron isotopes after irradiation can be extracted from the SIMS measurement and is presented on Figure 11. The ^{11}B count rate was used to quantify the variation of the ^{10}B content after the irradiation with the assumption that the ^{11}B content has not changed during the irradiation. The ^{10}B content in the specimen after irradiation in % of the initial content as well as the burnup are presented in Figure 12. From this curve an area averaged ^{10}B burnup value was calculated and compared with the value measured by (classical) inductively coupled plasma mass spectrometry (ICP-MS) from a neighbouring sample after dissolution, see Table II.

TABLE II. ^{10}B BURNUP DETERMINATION BY SIMS AND ICP-MS

	Isotopic concentration (atom%)		**^{10}B burnup (%)**
	^{10}B	**^{11}B**	
SIMS based ^{10}B burnup analysis	-	-	47 ± 2
ICP-MS burnup analysis on neighbouring sample	9.77	90.23	51 ± 0.5

5.2. Discussion

The applied SIMS analysis technique requests sample holder movements in front of the (stationary) secondary ion optical, electrostatical energy filter. The movement leads to variations in the electrical field strength and secondary ion extraction conditions, resulting in (with respect to the area) tilted count rate distributions. The ^{11}B normalization removes this problem and shows a symmetrical (cylindrical) ^{10}B distribution. Further secondary ion peaks of ^{3}H, ^{7}Li, ^{12}C and possibly also ^{4}He can be identified but are not discussed in this presentation.

The data presented in Figure 12 and Table 2 show that the technique leads to quantitative, local (and averaged) boron burnup results which can indeed be used to validate burnup models. The value of the technique is not limited to boron analysis as has been demonstrated by PSI in hafnium burnup and actinide distribution analyses on burnable poison and UO_2 and MOX fuel rods respectively [Ref 6 and 7]. Obviously such analyses could be introduced also for new absorber isotopes in discussion. Presently the error assessment is only qualitative and needs to be improved (e.g. by comparing in the future a ^{11}B normalization with a ^{12}C normalization). As indicated above, the distribution of lithium and tritium can be assessed as well. This analysis however makes sense only after improved (dry) sample preparation which will be tested next on full size dense boron carbide absorber samples.

6. SUMMARY

Several studies of failures in control rods have shown that the mechanism of cracks in stainless steel is IASCC. To avoid IASCC the most efficient way seems to be to remove causes for stresses in the component. If the absorber material can be designed not to strain the steel cladding, cracks will not appear in control rods under the nuclear life. Such an concept is to create a boron carbide pin of almost theoretical density where boron carbide densification is accomplished prior to operation. Modelling of the operational behaviour of pins is much easier then modelling of powder. By post irradiation isotope analysis in a cross section of the pins with techniques like SIMS, the modelling is improved. By using boron carbide pins without internal void it is ensured that the void, now allocated outside the body, is ensured for accommodation of swelling. Designing a control rod to avoid stresses is more readily done this way.

Management of control rods must be based on experiences from inspection programs. Examinations such as neutron radiography have been a valueble help to reveal the consequences of absorber material behaviour in case of water intrusion after cracks in the stainless steel cladding. Data shows that the B_4C losses are neglible in rods with cracks. Cracks can be allowed to appear under operation. Knowledge of the base-line tritium levels in the reactor under operation makes it possible to interpret peaks in the tritium levels, which can be used in the planning of control rod handling. A concept is studied at ABB Atom.

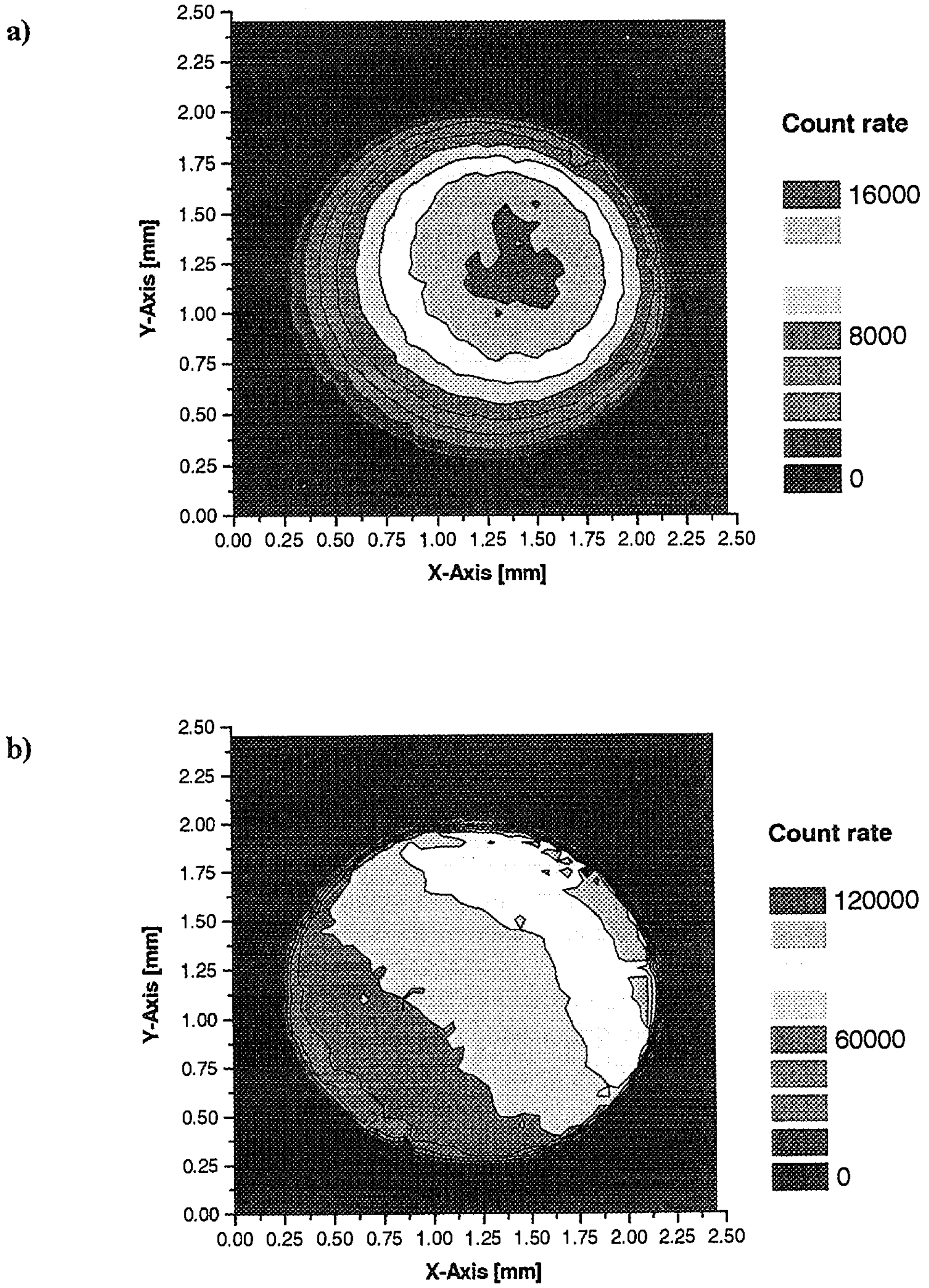

FIG. 10. SIMS area scan of the $B_{8.5}C$ absorber specimen (Raw data, not corrected, not normalised).
a) ^{10}B count rate distribution, b) ^{11}B count rate distribution

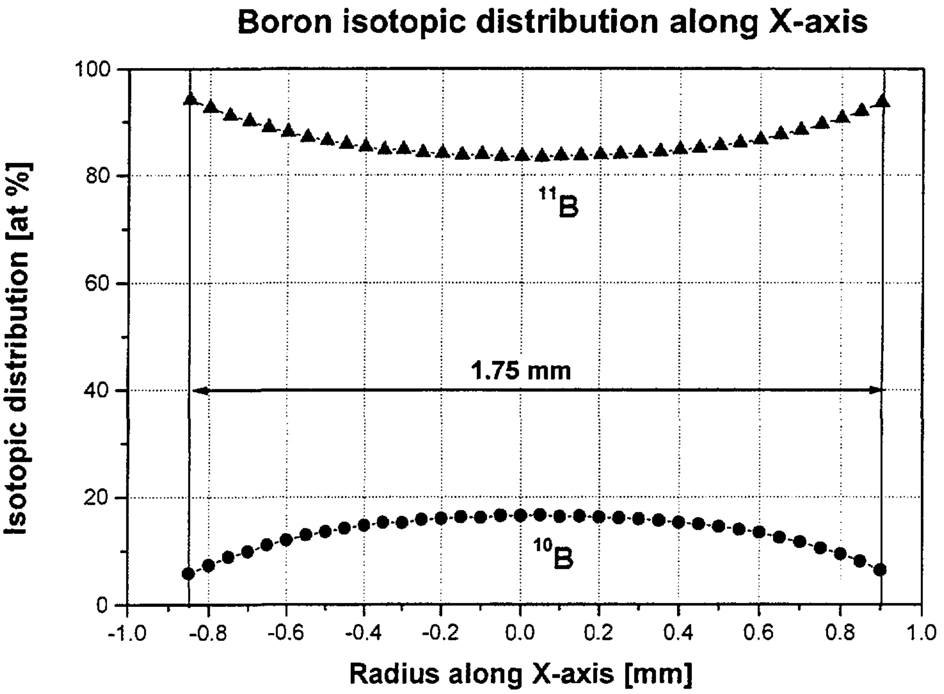

FIG. 11. Boron isotopic distribution along the X-axis of the specimen

(calculation : $Iso^{10}B(r) = \dfrac{cr^{10}B(r)}{cr^{10}B(r) + cr^{11}B(r)}$, $Iso^{11}B(r) = 1 - Iso^{10}B(r)$)

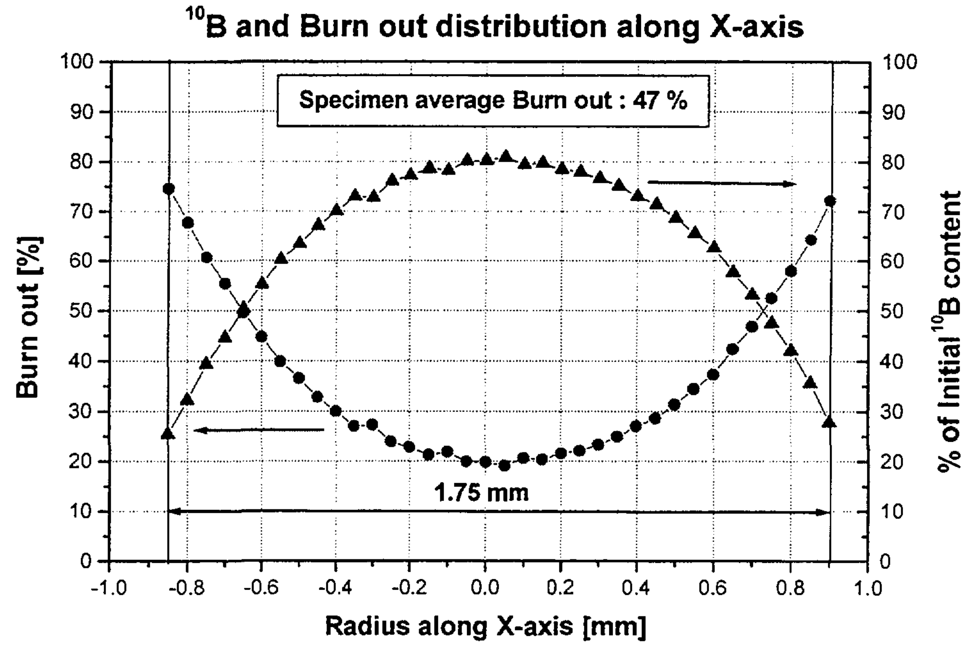

FIG. 12. ^{10}B content and burnup distribution along the X-axis of the specimen.

(calculation : $^{10}B(r) = \dfrac{cr^{10}B(r)}{cr^{11}B(r)} \cdot \dfrac{^{11}B_{initial}}{^{10}B_{initial}}$, $BU^{10}B(r) = 1 - ^{10}B(r)$)

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