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FRAMATOME CONTROL ROD ABSORBER MATERIALS: EXPERIENCE AND DEVELOPMENT

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Abstract

Phenomena limiting the lifetime of the RCCAs in PWRs have already been highlighted in the past. Wear of the rodlet cladding and swelling in the lower tip end of the cladding arising from the structural changes in the AgInCd absorber material are the two damage mechanisms encountered: wear, potentially leading first to cladding perforation secondly further later rod mechanical failure; and swelling, causing clad cracking and rod swelling possibly culminating in RCCA jamming in the fuel assembly guide thimble. The upgrades applied to the new generation HARMONI™ RCCAs have provided a solution to the RCCA wear problems and delayed contact between absorber and cladding. Better knowledge and prediction of AgInCd swelling in the reactor is necessary, however, as it conditions the lifetime of the RCCAs. An extensive analysis programme of this AgInCd absorber was undertaken by FRAMATOME in conjunction with EDF, in order to determine the causes of its out-of-pile and in-reactor changes (creep and metallurgical changes in the material under irradiation), predict its behaviour and make structural improvements limiting its in-reactor changes. The outcome of this analysis was the HARMONI™ 2G design featuring an improvement in the Ag-In-Cd material. Turning to the 1300 MWe RCCAs containing boron carbide (B_4C), an experiment on the behaviour of this absorber has been conducted in an EDF reactor. B_4C was inserted into claddings pre-perforated at the fabrication stage and subjected to corrosion by the reactor coolant. The first lessons on the conditions of boron carbide dissolution have been drawn. The improved knowledge in the behaviour of these absorbers in the reactor and the design enhancements made are allowing prediction of a lifetime with respect to swelling which is further extended for new generation HARMONI™ RCCA relative to the first HARMONI generation. A development programme on an RCCA design using hafnium absorber is also in progress. The use of hafnium would completely rule out swelling in the lower tip end of the RCCAs.

1. INTRODUCTION

Few years ago, FRAMATOME has developed a new RCCA product called HARMONI™ which definitively remedies cladding wear and offers a real improvement against swelling. The design of the HARMONI™ RCCA combines ion-nitriding anti-wear treatment of the cladding tube and several modifications such as reduction of absorber diameter along the lower part of each rodlet, helium backfilling of the rodlet and use of AISI 316L cladding for enhancing swelling/cracking resistance.

The accumulated in-reactor experience, under various operating conditions, confirm the adequacy of this design with respect to wear and swelling/cracking resistance. No indication of wear was detected on any rod in the ion-nitrided part on more than 1700 HARMONI™ RCCA in operation to date with approximately two thirds in EDF reactors. The maximum wear experience feedback of an ion-nitrided RCCA is seven 12 month cycles in 900 MWe and 1300 MWe EDF reactors (lead RCCA) and only four cycles regarding the clad swelling. Probably, the swelling/cracking phenomena will condition the lifetime of the HARMONI™ RCCAs design.

The HARMONI™ RCCA was the first result of a large-scale Research and Development programme undertaken to provide a second generation of HARMONI™ RCCA with higher performance regarding the phenomena limiting RCCA lifetime.

After a short recap of the swelling/cracking phenomena, this paper presents the extensive analysis programme of the AgInCd absorber behaviour under irradiation undertaken in conjunction with EDF to :

- understand the creep mechanism;
- determine the effect of AgInCd grain size on creep law;
- predict the AgInCd creep deformation rate;

- understand the swelling mechanism under irradiation (metallurgical changes in the material under irradiation);
- predict the swelling volume rate and diameter increase of AgInCd under irradiation.

The consequences of this programme on the HARMONI^{TM} 2G design, featuring an improvement in the AgInCd material and an increase of RCCA lifetime, are detailed. The improved knowledge of boron carbide (B_4C) behaviour subjected to water corrosion is also an important safety concern. The special experiment conducted in the PALUEL 2 reactor is described and this paper gives an outline on the conditions of boron carbide dissolution.

Lastly, a general idea of the development of a lead hafnium RCCA is presented; the use of hafnium would completely rule out swelling in the lower tip of the RCCAs if it is protected against hydriding and wear.

2. GLOBAL DESCRIPTION OF THE SWELLING/CRACKING PHENOMENA

Wear inspections on RCCA absorber rods have revealed swelling on several rodlets, sometimes combined with longitudinal cracking of the cladding at the bottom of the rodlet. The interpretation of this phenomena which is based on the findings in hot cell investigations of PWR 900 and 1300 MWe rodlets presented below, demonstrates:

- diametral and longitudinal variation of the absorber caused by creep under the effect of applied static and dynamic stresses;
- diametral swelling of AgInCd absorber resulting from irradiation-induced metallurgical changes.

These findings lead to the following conclusions about the cladding strain mechanism:

- at beginning of life, axial shortening of the absorber stack occurs under the effect of thermal creep, caused by the static and dynamic stresses applied to the absorber. The direct outcome of this axial shortening is an increase in absorber diameter and gradual reduction of the absorber-cladding gap. The thermal creep mainly governs the narrowing of absorber-cladding gap and there is progressive closure of this gap. When contact has occurred, creep stresses are not sufficient to cause cladding deformation;
- at the same time, under the effect of irradiation, the chemical composition of AgInCd is modified (transmutation of Ag into Cd and In into Sn) causing the beginning of swelling and occurrence of a second phase as soon as the solubility limits of Sn are overstepped. It leads to deformation of the cladding and to a local stress increase in the cladding;
- cracking occurs along a cladding generation line if the absorber pushing leads to exceed the cladding ductility which is itself linked to irradiation;
- after cracking, absorber creep resumes and is superimposed on irradiation swelling.

Figure 1 illustrates the effect of the absorber diameter evolution versus time but in reality, the phenomenon is more complex and this variation is not fully linear since it is influenced by:

- the operating mode, which influences RCCA insertion and therefore the heat-up and the fluence seen by the materials;
- the spatial distribution of absorber-cladding gap (the off-centering of the absorber in the cladding and the progressive closure of the gap contributes to a drop in temperature);
- the changes in the absorber grain size due to temperature effect;
- the changes in mechanical properties (such as lower thermal conductivity) arising from those in the chemical composition and its structure.

Better knowledge of AgInCd creep and swelling and prediction of creep and swelling rates are however necessary as they condition the lifetime of the RCCAs.

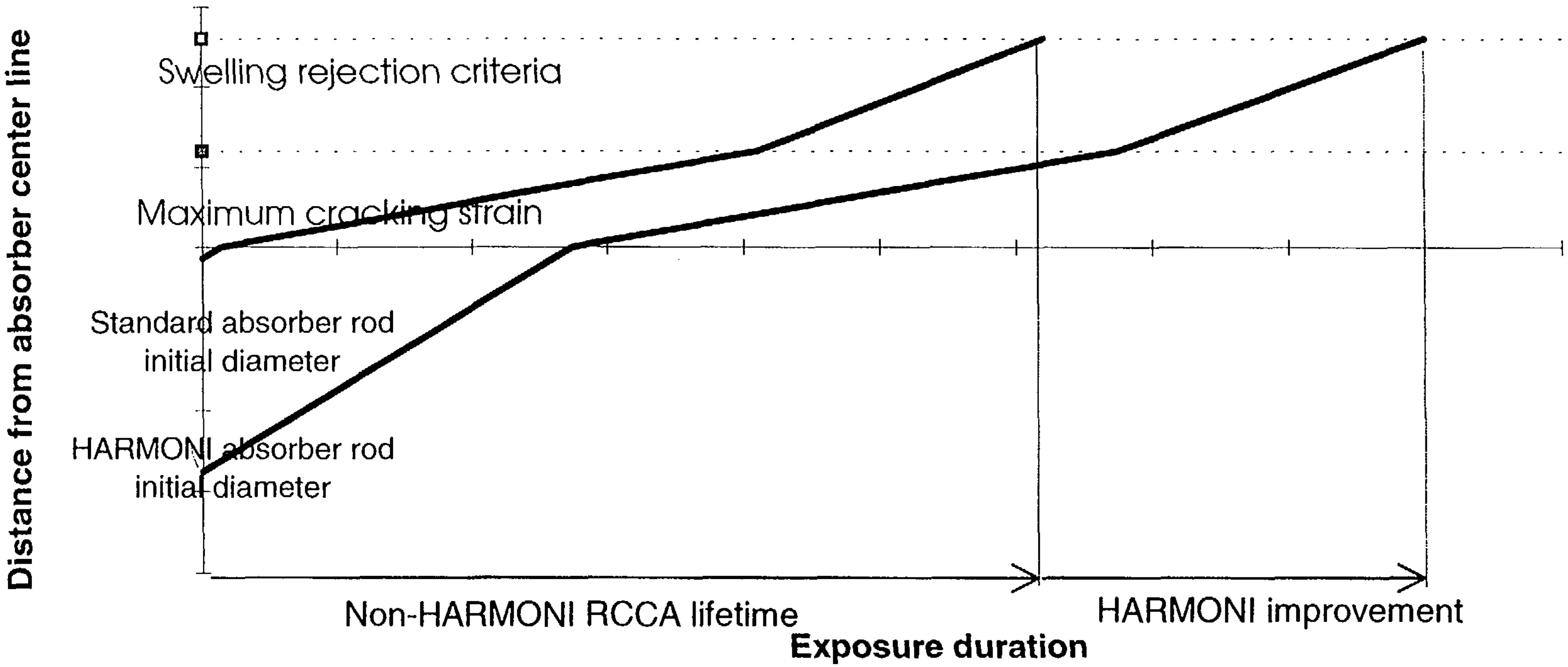

FIG. 1. Absorber-clad gap evolution versus time

3. AgInCd CREEP ANALYSIS

To understand AgInCd creep and determine its thermal behaviour and creep, FRAMATOME launched an extensive programme of thermal analysis and creep tests.

3.1. Thermal behaviour of AgInCd absorber

This first phase of the investigation programme was to understand the out of pile behaviour, specially with a constant temperature. When the AgInCd material is subject to high temperature above half melting temperature (Tm/2=260 C) or recrystallization temperature (about 275 C), the grain size increases by recrystallization then the grain coarsening continues. This evolution depends on the initial grain size, the material temperature, the cold working rate and the time.

FRAMATOME ran a series of tests to measure the grain size trend for AgInCd materials which initially had a grain size included between a "small grain" size ASTM 6-8 (between 20 and 45 microns) and a "large grain" size ASTM 0-2 (between 170 and 355 microns) depending on:

- the in-reactor temperature of the material;
- the hold time.

This thermal study showed that there was no significant change of this grain size up to 350 C and for higher temperatures this change is smaller in scale with a large grain material. Grain size measurements on RCCA rodlets irradiated 8 and 9 cycles in reactors have confirmed that there was no major change in the grain size in the out-of-flux zones. As a result, the absorber-cladding gap has the time to be closed by in-reactor creep with a low grain size material before grain coarsening occurs.

3.2. Creep test programme

In order to determine both the thermal creep mechanism and a law of behaviour of the irradiated material versus the key parameters, FRAMATOME has undertaken a large-scale creep test programme on Ag-In-Cd materials in different metallurgical states and covering a wide range of initial grain sizes. 54 creep tests were run on standard specimens machined from fabrication bars for tensile creep tests or from specimens cut directly from fabrication bars for compressive creep tests more representative of the in-service loadings.

The test parameters were considered so as to be representative of the range of actual in-reactor loadings (several temperatures and stresses applied to the absorber drawn from the operating conditions) and with several grain sizes ranging from ASTM $\leq$ 0 to ASTM 8. The measurements taken on a continuous basis consisted of measurement of the axial deflection of the plates applying the force, giving a deformation/time curve and grain size measurements after testing for assessment of material changes. Figure 2 shows an example deformation/time curve obtained by creep with a temperature of 350 C and a stress of 3.5 MPa.

Irrespective of the initial grain size, all the tests show a creep rate trend which can be split up into:

- a period of 0 to 160 - 200h corresponding to primary creep;
- secondary creep at a rate diminishing in steps for test temperatures 350 C.

The grain size measurements confirmed that the secondary creep trend is dependent on the grain size growth during the test.

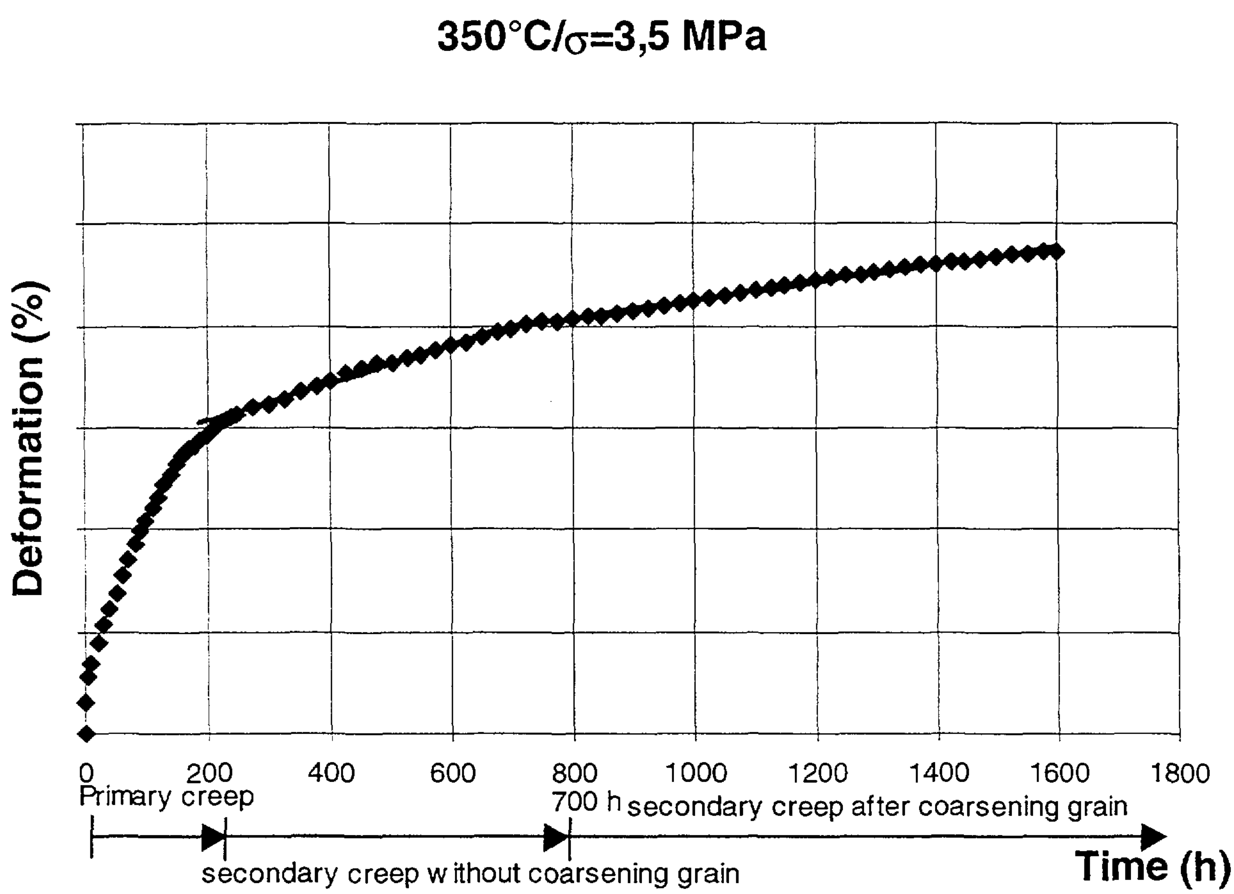

FIG. 2. Typical AgInCd thermal creep

3.3. AgInCd out of pile creep law

As primary creep is short in duration < 200h, only a formula for secondary creep rate $\dot{\varepsilon}$ measured experimentally was sought versus the parameters stress, temperature, grain size and time, in the standard form:

$$\dot{\varepsilon} = K\, d^{n}\, \sigma^{m} \exp - \frac{Q}{RT}$$

where:

$\dot{\varepsilon}$: creep rate
K, n, m : constants
d: pre-creep grain size in microns
 : stress in MPa
Q: creep activation energy in Joule/mole
R: ideal gas constant
T: temperature in Kelvin.

A simplified way of taking into account grain coarsening was applied by discretizing the law into a short-term law (< 700 h - Figure 2) and a long-term law (> 700 h); the long-term law implicitly allows for growth through coefficients Q and K.

The results show creep rate dependence on stress not constant with the grain size and a creep rate inversely proportional to the initial grain size of the material. The creep activation energy is fully comparable with that of the diffusion of pure silver along the grain boundaries for the short-term law. This activation energy is drastically reduced when the test duration lengthens, showing the effect of grain growth.

3.4. Creep mechanism

The interpretation of the coefficients n, m, Q of the creep laws was performed by comparing them with the creep laws of pure silver in the domain of "high temperature" (> melting point/2) and low-stress. The coefficients obtained for a test duration shorter than 700h correspond to a plastic strain mode controlled by the diffusion of atoms along the grain boundaries (COBLE creep [1]) although Ag-In-Cd is a solid solution with major dilution.

3.5. Consequences

These tests showed that an AgInCd material with large grains (ASTM < 3) drastically reduces the creep rate (Figure 3) relative to the material previously used (ASTM 6-8) by a factor 5 to 10 and afterwards extends the absorber/cladding gap closure time in the period during which absorber creep predominates over irradiation-induced swelling.

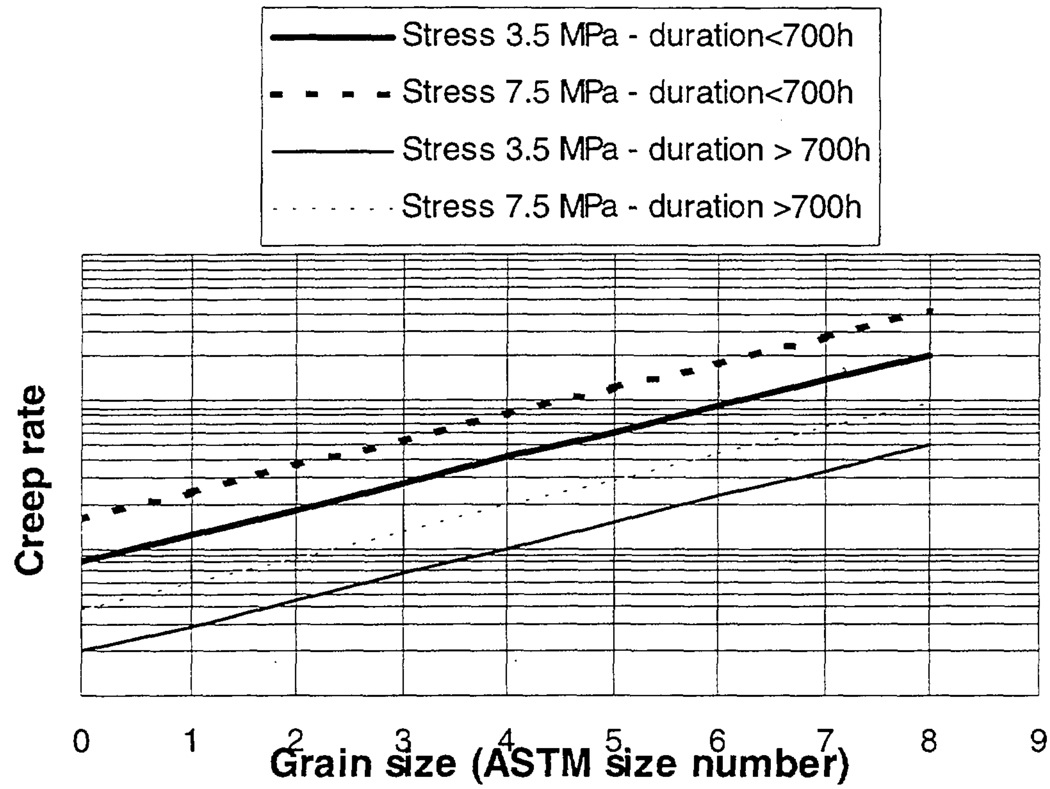

FIG. 3. Grain size effect on creep rate

4. AgInCd SWELLING ANALYSIS

4.1. Examinations of irradiated AgInCd bars

To determine the swelling mechanism of absorber rods and to model the swelling kinetics, FRAMATOME and EDF co-operated in a hot cell expert assessment programme using rodlets from 900 and 1300 MWe reactors.

This programme measured the diametral swelling and absorber density trend in three 900 MWe RCCAs and four 1300 MWe RCCAs from different banks (control, shutdown, power compensation), making eleven swollen rodlets. It was supplemented by a programme characterizing the structure and the modifications made under irradiation [2] with the aid of optical microscopy, microanalysis, metallographs and X ray diffraction measurements (performed by the CEA), especially on one AgInCd bar irradiated 8 cycles in reactor.

These examinations showed in the first place that the density or volumetric swelling of the absorber changes linearly with irradiation up to a given fluence (Figure 4). Figure 4 also shows that beyond this limit fluence, the change remains linear but with a steeper slope.

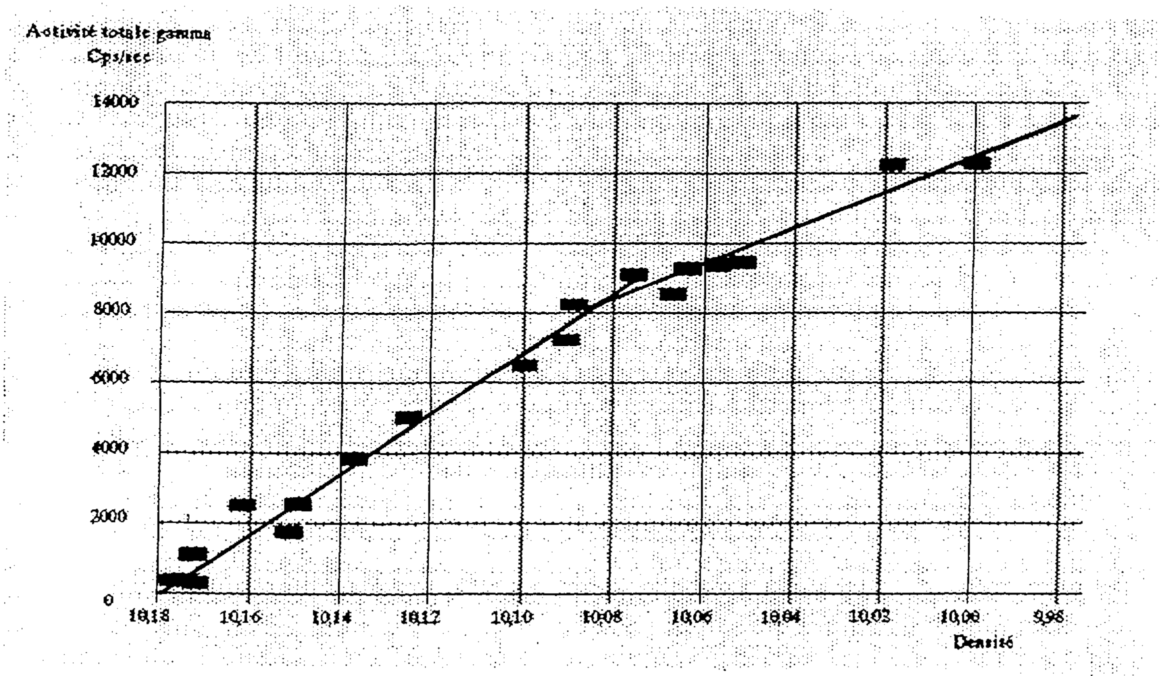

FIG. 4. Gamma rod activity versus AgInCd density

4.2. Swelling mechanism

The metallographs performed on a few samples confirm this difference in behaviour:

- up to a dose limit, the microstructure is principally single-phase face-centred cubic (fcc). During transmutations from Ag into Cd and from In into Sn, the atoms created are more voluminous and are soluble in the fcc network so there is swelling by a transmutation effect;
- beyond this dose, the solubility limit of the elements Cd, In, Sn is exceeded. There is occurrence of a close-packed hexagonal phase (hcp) more voluminous than the initial fcc phase. The structure is then principally two-phase (fcc + hcp) but at the periphery only the hcp phase can be obtained [2].

The additional analyses [2] determined a solubility limit on the order of 1.7 to 2 at.% tin in the fcc phase and a minimum 4 at.% tin in the hcp phase.

However, on a sample from a bar temporarily subjected to high flux, the X ray analyses evidenced the presence of singular zones highly enriched in tin up to 34%. These small-sized zones seem localized at the junction points of second-phase domains. This existence cannot be explained by global oversaturation of the material in tin, as the fluence received is not sufficiently high to cause such an enrichment and the micrographs reveal little hcp phase. These findings show the importance of the role of transmutations in the material structural changes and justified the need to closely investigate the AgInCd quarternary system to:

- gain greater insight into the phases forming under irradiation;
- predict the proportion of each of the phases in the material;
- simulate the development of the concentration profiles of the elements within the two phases.

This led to a joint FRAMATOME/CEA research programme as presented in 4.4. The aim of this programme is to simulate the growth of a hcp phase precipitate on an fcc phase grain boundary in the absorber and thus to finally predict the irradiation-induced swelling in the hcp phase. The swelling in the fcc phase is deduced by the Zen law [3] using the effective atomic volumes of the elements.

4.3. Swelling modelling

Based on the density measurements taken during examinations, a macroscopic model of AgInCd irradiation swelling was built, with allowance for the accelerating effect arising from the occurrence of the hcp second phase. For each examined irradiated RCCA, the volume variations along the absorber (calculated from the density measurements) were correlated with a distribution of fluences calculated on this absorber and adjusted to the values obtained from the gamma activities measured on two RCCAs. A fine fluence calculation was also carried out on a reference RCCA, for which all the insertions were recorded during the cycle.

In the case of RCCAs from temperature control bank R, the overall calculation method overpredicts by about 25% the value estimated by the measured activities. By refining the method with the reference RCCA whose every insertion is known, the accuracy of the fluence calculation improves. Should the absorber be inserted into the fuel stack, the uncertainty obtained does not exceed 11% even for an RCCA frequently in motion (power compensation bank G). The density measurement accuracy leads to an uncertainty on the volume variation measurement on the order of 10 to 20%.

A two-slope swelling model was thus determined by means of linear regressions for the experimental points lying on each side of the hcp occurrence fluence. Figure 5 shows the nominal law obtained, as defined in the neutron energy range of 0.625 - 3 eV corresponding to indium -> tin transmutations, with the experimental points. Good agreement is obtained and minimum and maximum laws bounding swelling were determined.

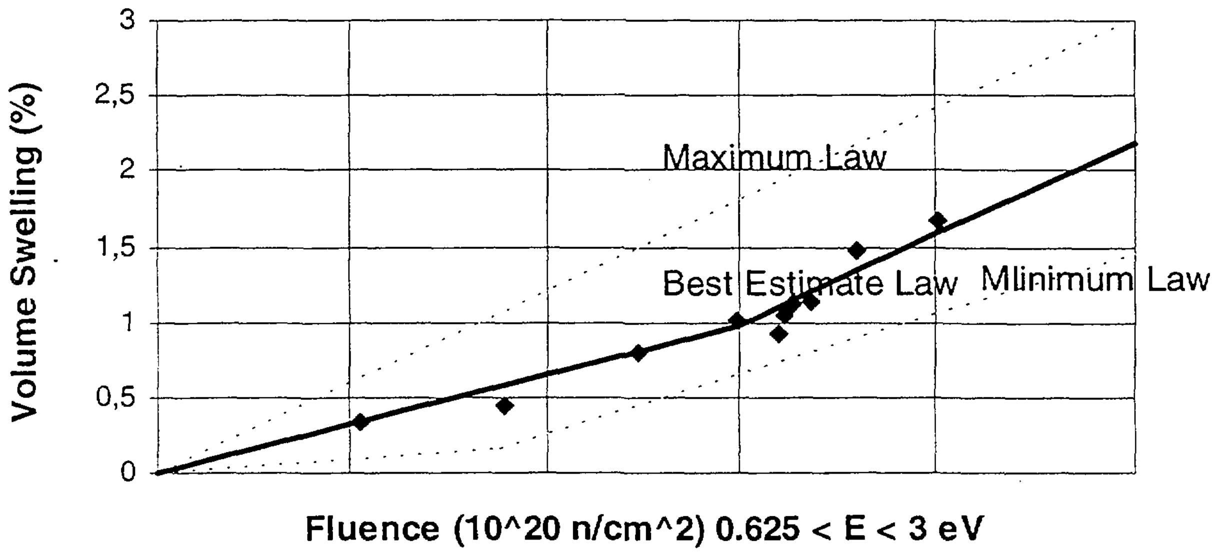

FIG. 5. Swelling rate versus fluence

Application to the swelling calculation was performed by considering an isotropic swelling of the absorber as long as there is no contact with the cladding. Processing of examination results for cracked rodlets with hard contact of the absorber and cladding (absorber bar diameter change and density measurements) leads in this case to non-isotropic swelling.

An evaluation of the increase in diameter of the absorber during an annual cycle was conducted with this law and compared with the experience feedback from cladding average swelling measurements determined by UT inspection. The calculated value of 21 microns/cycle for bank R is consistent with the average swelling value (19 microns/cycle) obtained for the set of measured RCCAs ; i.e more than 500 RCCAs.

The combined use of these absorber creep and swelling laws in one absorber rod thermal-mechanical computation software programme, allows prediction of the pre-contact time of the absorber and the change in clad swelling after hard contact with the absorber.

4.4. Modelling of AgInCd composition under irradiation

A wide-ranging research programme was run to understand and model the phase transformation processes in the absorber. In particular, the change under the effect of the transmutations of the concentration profiles within the two phases as soon as an hcp phase precipitate exists and the determination of the proportion of each of the phases allows evaluation of the quaternary absorber material swelling. The laws of variation of atomic volume with chemical composition in both phases was also determined from representative synthetic alloys.

For this purpose, this research relied upon two preliminary studies:

- study of the growth of a precipitate under the effect of the transmutations in the simple case of a binary alloy Ag-Cd [4];
- quantitative modelling of the phenomena of diffusion through the quarternary alloy for both phases [5].

These studies showed that the enrichment in transmuted element at the centre of the mother phase and of the precipitate occurs to the detriment of the growth of the latter as soon as the transmutation rate (neutron flux) is large compared with the mobility of the atoms. It is all the larger when the flux is high and the diffusion coefficients are small. This can give excessive oversaturation in elements at the core of the precipitate, as already experienced for tin.

The effect of increasing the absorber grain size has been looked at. As a result of the diffusion coefficients in the hcp phase which are greater by about 10 than those obtained in the fcc phase, there is no effect of increasing grain size on the second phase precipitation.

4.5. Consequences

Based on the knowledge of the neutron flux and of the axial force exerted on the absorber, the use of the full-scale swelling model in conjunction with the thermal creep model makes it possible to predict changes in absorber/cladding gap closure and subsequent clad swelling. The favourable effect of the increase in grain size on creep is maintained under irradiation. Changes in the chemical composition of the absorber were also evidenced, with the aim of supplying if necessary a further lifetime gain by delaying the occurrence of the second phase.

5. NEW HARMONI™ 2G RCCA

5.1. Description

The new RCCA generation HARMONI™ 2G incorporates an AgInCd absorber material with modified grain size. A new grain size value (ASTM < 3), i.e. a grain diameter greater than 120 microns (instead of 30 microns for the standard material) is thus obtained and it is verified, through a controlled fabrication process, that there will be no recrystallization risk during operation. The HARMONI™ 2G RCCA presents all the benefits of the HARMONI RCCA and even more regarding the AgInCd deformation which leads to an increasing of lifetime.

5.2. Absorber rod diameter evolution

The principle of Figure 1 can be retained to measure the characteristic RCCA lifetime gain supplied relative to the former design with "small grain" absorber (Figure 6). The decrease in absorber thermal creep through the increase in its grain size provides a significant reduction in the absorber/cladding gap closure kinetics at BOL at the time when the stresses and temperatures are high. The use of "large grains" has no effect on the swelling under irradiation or on the other properties and characteristics of the absorber.

During lifetime and before hard contact with the cladding, this advantage tends to diminish since the temperatures and stresses remain higher with the large grain material because of the slower change in the bar dimensions. This effect has been analyzed and is negligible compared to the gain supplied by the increase in grain size (Figure 6). After the phase of hard contact with the cladding, the time gain is therefore kept for the swelling phases (Figure 6).

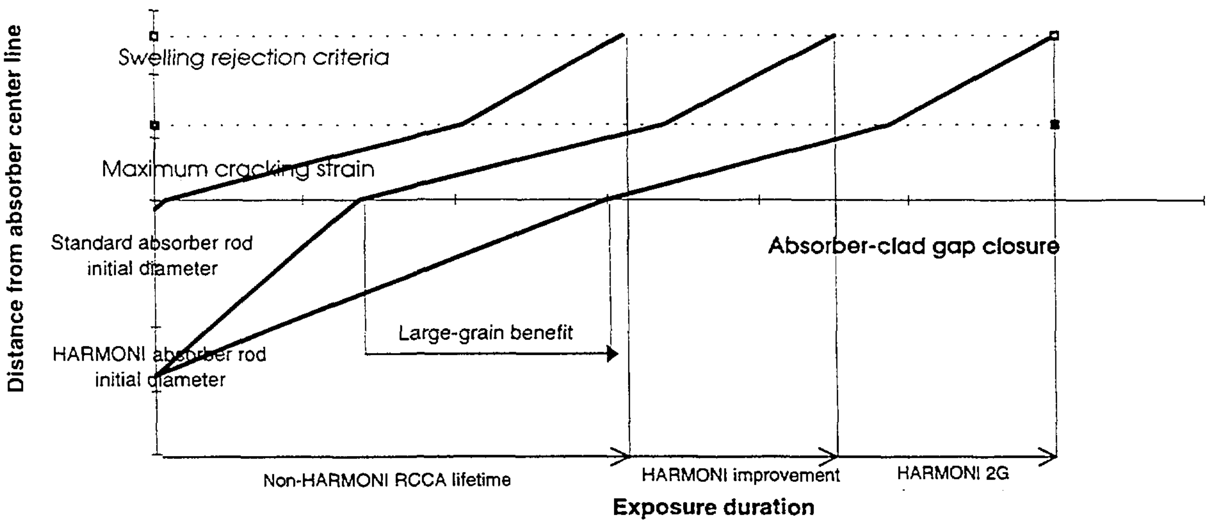

FIG. 6. Grain size effect on absorber-clad gap evolution

6. BORON CARBIDE BEHAVIOUR UNDER WATER CORROSION

6.1. Experiment facility

All the experiments performed to characterize the leaching behaviour of B_4C, used in conjunction with AgInCd for the black 1300 MWe RCCAs, have been conducted in autoclave non representative of in-reactor water corrosion or with Al_2O_3- B_4C pellets different from the 1300 MWe design [6], EDF and FRAMATOME decided to launch an in-reactor experiment with two purpose-built RCCAs.

The experiment was conducted with B_4C inserted into cladding tubes pre-perforated at the fabrication stage for a few rods of two RCCAs in order to represent through-wall wear in reactor (guide card location or bottom tip wear). These two RCCAs have been inserted in PALUEL 2 plant in R bank (subjected to a constant neutron flux). The first (named A) was withdrawn after one cycle and the second (named B) after three cycles .

The RCCA A uses two pre-perforated rods, the first with an oblong hole of 3 mm width and 10 mm long positioned at the bottom of the B_4C stack made to look like guide card wear and the second rod with a 3 mm diameter hole at the bottom of the rod (25 mm above the bottom end of the cladding tube) to simulate a tip wear. The RCCA B uses the same bottom pre-perforated rod as the A one.

These purpose-built rods are designed with a special AgInCd bar of 492 mm height in place of the 1016 mm classical bar. This was performed to obtain a high B^{10} depletion rate (approximately 4.10^{20} destruction per cm^3 for a twelve month cycle). These rods have been characterized at the fabrication stage like pilot rods located symmetrically to those on each RCCAs and a complete recording of the RCCAs axial positions was carried out.

6.2. Main results

The non destructive Eddy Current inspection of RCCA A at the end of the first cycle showed a drop of the spring location and a B_4C loss of 500 mm height was measured for the perforated oblong hole rod. For the other one, no B_4C column evolution was detected.

The hot cells examinations on RCCA A confirmed this assessment and showed the damages:

a) perforated oblong rod

- loss of 523 mm of the B_4C stack;
- peripheral degradation of some B_4C pellets (decrease of the limited to 7 % of the pellets stack;

b) bottom holed - rod

- no height loss of the B_4C stack;
- peripheral degradation of 10% of the stack..

The experiment will continue in 1999 with the hot cells examinations on the RCCA B after three cycles.

6.3. Consequences

These in-reactor results show that leaching and erosion during the RCCA stepping together with the primary water media have partially affected B_4C pellets subjected to :

- a sufficient B-10 depletion (above a threshold);
- a water circulation around the pellet.

All the 1300 MWe black RCCAs are implemented with the classical 1016 mm AgInCd bar, so the B_4C pellets of RCCAs shutdown bank rods are out of irradiation or like the R bank received a small burn-up. There would be no loss of B_4C height for the usual RCCAs because the B_4C stack dimension of these classical RCCAs is in fact 524 mm greater than the tested rod stack. A prolonged irradiation exposure of bank R RCCAs could involve a small peripheral degradation of the first B_4C pellets without harmful consequence on the RCCA reactivity feedback.

7. HAFNIUM RCCA DEVELOPMENT

The design enhancements made in the HARMONI™ 2G RCCA may allow a further increase in lifetime with respect to swelling but the swelling phenomena are not ruled out. This new design allows a less frequent control of the RCCAs due to the significant reduction of the absorber-clad closure rate. The swelling lifetime of such a RCCA is not yet equivalent to the potential wear lifetime.

The hafnium absorber has a neutron worth equivalent to the AgInCd one with identical dimensions and benefit from several advantages :

- no swelling under irradiation;
- no creep behaviour (melting temperature near 2200 C);

- acceptable behaviour under accident conditions due to its high melting temperature;
- constant neutron worth during their lifetime;
- possibility to use hafnium rod without clad (owing to the fact of its excellent behaviour under primary water corrosion) and then to extend the global RCCA reactivity feedback.

FRAMATOME has decided to design hafnium RCCAs. Demonstration of new hafnium RCCAs in reactor will be implemented in EDF reactor.

8. CONCLUSION

The better knowledge of the behaviour of the absorbers present in the in-reactor designs at this time and the improvements made by the new HARMONI™ 2G generation are allowing an extension of RCCA lifetime with respect to the swelling phenomenon. The modelling of the phenomena and its comparison with experience feedback will make it possible to offer a better prediction of this swelling. This enables the RCCA maintenance strategy to be adapted and the potential risks arising from unpredicted RCCA swelling to be limited. Analysis of the clad perforation risk in the presence of B_4C also makes it possible indirectly to extend the lifetime of the RCCAs of previous designs (possibility of accepting perforation).

The use of hafnium to rule out the swelling phenomenon and to offer a substantially longer lifetime is being experimentally investigated.

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