A THEORY DIRECTING INVESTIGATION OF SAFETY OF NUCLEAR MATERIALS UNDER IRRADIATION CORROSION ENVIRONMENT

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ABSTRACT

Although the subject of irradiation corrosion has been studied for more than 39 years, there is not yet a general theory universally accepted. In this paper, in virtue of the realization of the monovalue ion energy by accelerator, a parameter G, the irradiation corrosion damage efficiency, was defined theoretically. A W-shaped curve of the G-D function was established by using zirconium alloy samples bombarded with Zr^+ and Ar^+ ions respectively and then tested electrochemically in LiOH water solution at high pressure and high temperature, in H_2SO_4 or H_3BO_4 water solution at room temperature etc. With this curve, the whole process of irradiation corrosion was divided into 6 stages i.e. primary oxidation, enhancement of irradiation corrosion, saturation, decrease and reversing into the protection zone, saturation of protection, and final decay. This curve reflected change of most parameters in irradiation and electrochemical polarization, and presented a comprehensive explanation of mechanisms of irradiation corrosion process. This curve unified the contradictory experimental results in the history up to now and the different opinions between laboratory investigations and engineering data and experiences. The applications of this theory was expected: 1) to evaluate the irradiation corrosion resistance of materials; 2) to direct the establishment of the data base of irradiation corrosion of different nuclear materials and establishment of the correlation between ion irradiation corrosion and the neutron irradiation corrosion in different reactors; 3) to help the subjects in other application areas involved irradiation and corrosion of materials e. g. space navigation etc., and 4) to direct the experiments of simulation of neutron irradiation corrosion by ion bombardment.

INTRODUCTION

The phenomena of decay of materials under irradiation exist in many application areas such as nuclear power plants, astronautical navigation, semiconductor industry etc.. The extensive investigation of the corrosion behavior of materials under irradiation inside nuclear power plants began more than 39 years ago[1,5] as a leading subject in company with the whole development process of nuclear industry. The success of the operation of nuclear power plants partially owned to the successive achievements of the studies of irradiation corrosion. As a negative instance, the failure of the engineering operation of melted-salt nuclear power plants were mainly due to the un-solution of the irradiation corrosion of nuclear materials in this kind of medium.

Most important engineering data of irradiation corrosion of zirconium alloys in Pressurized Water Reactors (PWR) and Boiling Water Reactors (BWR) were achieved during this long period of investigations. In 1985, Canada (by B. Cox et al)[2] published its engineering data entitled "Assessment of PWR waterside corrosion models and data”. In 1987, the northwest laboratory (by A. B. Johnson et al)[3] of USA published its final report entitled "Zirconium alloy oxidation and hydriding under irradiation ". And in 1992, International Atomic Energy Agency (IAEA) (P. K. Mathur et al)[4] published its technological document entitled "Coolant technology of water cooled reactors". Canada, USSR, France and Japan etc. have gotten successful operations of their nuclear power plants for several ten years. But the theoretical research work is still in its difficulties and fragmentary states.

Early in 1968, B. Cox [5] had a review of the engineering and research aspects of irradiation corrosion in nuclear power plants. He gave the preliminary model of the irradiation on the electro-chemical polarization curve and was conscious of the dose saturation of irradiation corrosion, but all of these were too primary to form a general theoretical model to describe the whole process of irradiation corrosion. He wrote in conclusions: "what are needed are carefully controlled experiments which include sufficient variables to permit some elucidation of the mechanism."

In 1977, E. Hillner[6] have an overview of "Corrosion of Zirconium-Base Alloy" in which a engineering oxidation model including pre- and post-transition stages was reviewed, but the factors of irradiation and oxidation were not separated. He wrote in his conclusions: "In the absence of such hypotheses, we will be relegated to operating our reactors within the bounds of our own limited experiences. The inability to predict corrosion behavior for conditions beyond our experience may hamper seriously future dissimilar design applications. Whether or not a unifying theory for corrosion mechanism can be developed in the near future remains to be seen; however, this author believes that it should always remain our major goal in all corrosion studies."

In 1991, A. I. A. Almarshad et al[7] gave a semi-experiential model as follows,

$$\frac{X'}{X} = \frac{C_0 + U(M\Phi)^p}{C_0} \quad \text{..} \quad (1)$$

where x' and x are the thickness of oxide films with or without neutron irradiation respectively, Φ is flux ratio of neutron, and C_0, U, p and M are all constants. Though the calculation results were pretty agreed to those of experiments, the model was still lack of the understanding of the irradiation corrosion in concepts and was still in engineering and experiential level.

The main difficulties in the theoretical research of irradiation corrosion were that the factors affecting the irradiation and corrosion were too many to be separated, especially in the reactors. So that the whole history, so far, of irradiation corrosion research in reactors was almost limited on the level of engineering, which indicated that the separation of variables and the establishment of the new reasonable parameters has become the key problem of the research of irradiation corrosion.

Ion implantation has been used to simulate the effects of neutron irradiation on the mechanical properties of materials since 1960s[8]. After a long period of large quantity of experiments and arguments about its reasonability, the Silkeburge Meeting by International Energy Agency(IEA)[9] gave a positive and systematic summarization of this method. It was believed that the damage rate of materials by ion irradiation is 4-6 order of magnitude higher than that by neutrons ,and the accelerator could separate the irradiation parameters and get a better control of them. It is a promising way to use the ion implantation method to simulate the neutron irradiation corrosion to understand the effects of the relative factors inside the reactors on the corrosion of nuclear materials and to develop the irradiation corrosion theories.

The simulation of irradiation corrosion by ion implantation etc. involved many key problems such as how to confirm the implantation parameters, how to choose the expression parameters of irradiation and corrosion, how to choose the corrosion method and medium etc.. All of these problems are still in the darkness and are looking forward to a general theory which can bring the reasonable answers.

In this paper, the Zr^+ ions generated from 400keV accelerator, as the self-ions of Zirconium alloy, as well as Ar^+ ions were implanted into this alloy to simulate the pure damage process of neutron irradiation inside the reactors. Electrochemical anodic polarization was adopted as the corrosion monitoring method. The ion energy was controlled at a monovalue. The damage efficiency function of irradiation corrosion was deducted, simplified and the damage efficiency G of irradiation corrosion was defined and was expressed by the increment of anodic passivation current density after ion irradiation. The relationship between G and the implantation dose D was built up. The G-D curve appeared as a W shape and 6 stages of single value relationship of G on D were revealed and all of the irradiation parameters and corrosion parameters as well as all of the irradiation corrosion stages and mechanisms were concentrated into one figure. By this model, many contradictory experimental results were unified, the different opinions between experimental investigators on irradiation corrosion in laboratory and those in engineering were unified and the prospect applications of this model both in experiments and in industry are positively discussed.

EXPERIMENTAL

Samples

The samples of zirconium alloy were machined to 10mm x 10mm x 1.5mm for electrochemical anodic polarization at room temperature, and tube samples of (6mmx20mmx1.5mm) for that in LiOH water solution at high pressure and high temperature, from a sheet and a tube separately with completely recrystallized by vacuum annealing. The composition of the alloy is: Zr:in balance, Sn: 1.4 wt.%, Fe: 0.23wt.%, Cr: 0.1wt%, Ni: 60E-6, Al<14E-6, Ti<14E-6, Co<E-6, Mn<14E-6, Mg<14E-6, Pb<14E-6, W<10E-6, Mo<20E-6, Cu<20E-6, Si<50E-6, Cl<200E-6, N<30E-6, O<900E-6, H<10E-6, Hf<100E-6, B<0.5E-6, Cd<0.5E-6. Samples were abraded with sand paper of 300, 500 and 800 grit of SiC, degreased in acetone and ethanol, chemically polished in the solution of HF:HNO3:H2O = 10:30:60 in volume, rinsed in natural water not less than 3 times and finally washed with deionized water.

Ion implantation

The parameters of Zr^+ or Ar^+ bombardment were: ion energy of 190keV, dose of 2E15 to 8E16ions/cm^2, dose rate kept at 9.65E12ions/cm^2/s, in room temperature or liquid nitrogen temperature and a vacuum level better than 1.33E-3Pa.

Electrochemical

Irradiation and corrosion processes are all events in the surface layer of materials, whereas, the electrochemical measurement is just very sensitive to the surface changes, and so, just suitable to the irradiation corrosion monitoring.

<u>The choice of medium.</u> Because of the very shallowness (less than 300nm) of the irradiation range on the surface of samples, the corrosive of the medium must not be too strong otherwise the whole irradiation range would be corroded away before the starting of the electrochemical polarization. On the other hand, if the medium is too weak the whole corrosion process could not appear.

<u>Electrochemical at high pressure and high temperature.</u> Electrochemical polarization in LiOH water solution at high pressure and high temperature was conducted in reference to the operation condition of PWR, the medium parameters were chosen to be 300^{o}C, 8.08E7Pa, concentration of LiOH: 3.0E-6 Mole and the scanning speed of potentiodynamic anodic polarization: 5mV per second.

Electrochemical in room temperature. The room temperature was 19.3-24.6°C and the concentration of H_2SO_4 and H_3BO_4 water solution were 1N and 3.0E-6 Mole, the scanning speed was the same as that in 3.2.

THEORETICAL

The definition of ion irradiation corrosion damage efficiency function G

The key problem of the theoretical research of irradiation corrosion is how to find the valuable and reasonable parameters to build up the relation between irradiation and corrosion. The irradiation mechanism, as an old branch of physics, has been developed extensively, especially by J. lindhard, G. L. Kulcinski[10].

The displacement of the lattice atoms of the target materials by the incident particles could be expressed by the parameter of dpa (displacement per atom) as follows,

$$Cd = \varphi \bullet t \bullet \int_{Ed}^{\Lambda Ei} \sigma(Ei, E) \bullet \gamma(E) dE \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

where Cd is dpa, φ is the flux density ratio, t is irradiation duration, φ t=D is the dose, Ed is the displacement threshhold energy of the lattice atoms of target, ΛEi is the maximum transmission energy, σ(Ei, E) is the collision cross section where Ei and E are the energy of incident particle and the transmission energy of the lattice atom separately, γ(E) is the number of displacement of lattice atoms by the PKAs (Primary Knock Atoms) produced by an incident particle.

In a large quantity of literature on the effects of irradiation on the mechanical properties, the parameter of dpa was commonly adopted to depict the relation between the change of mechanical properties and the irradiation. In the early work of our group, the function relation was once built up between the increment of the passivation current density or the increment of oxidation weight gain and dpa[11]. It was found that these two kinds of increments were all in linear proportion to the dpa. These results were in accordance with the relation between neutron dose and the oxidation weight gain[6].

However, this kind of relationships were actually unreasonable. The events of the displacement process of the lattice atoms took place within about 10^{-11} seconds which were only relative with the parameters of incident particles and the lattice atoms, whereas the defect formation process took place, at least, within about 10^{-3} seconds[10] which were relative to the thermal diffusion, dislocations and crystalline boundaries in materials and the dose rate etc., and could last even several months. So that the displacement parameter dpa can not express the final damage results. Further more, not all kinds of damage defects affected a special corrosion property of materials. Y. S. Lee et al[12] found that the proton irradiation drove the precipitates inside zirconium alloys decomposed, which enhanced the uniform corrosion and reduced the nodular corrosion.

In 1969, W. N. Mcelroy et al [13] used the semi-experiential method to calculate relation between the change of a certain mechanical property index and the neutron irradiation in nuclear reactor. A defined quantity Gi(En) called damage function was defined as follows, suppose that some property index "i" changes in directive proportion to dpa i.e. Cd,

$$\Delta P_i = f_i \cdot C_d , \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3)$$

combined (2) and (3):

$$\begin{aligned}\Delta P_i &= t\cdot\int_0^{E_n^{max}}\psi(E_n)\cdot f_i\cdot\int_{E_d}^{\Lambda E_n^{max}}\sigma(E_{n,}E)\cdot\gamma(E)dEdE_n\\ &= t\cdot\int_0^{E_n^{max}} f_i\cdot\sigma_d^{tot}(E_n)\cdot\psi(E_n)dE_n\end{aligned} \quad .... (4)$$

where $\psi(E_n)$ is the flux spectrum of neutron inside the reactors. Considering the energy of thermal neutron, the lower limit of the integral is taken as zero. The total displacement cross section,

$$\sigma_d^{tot} = \int_{E_d}^{\Lambda E_n^{max}}\sigma(E_{n,}E)\cdot\gamma(E)dE \quad .... (5)$$

if the damage function is defined as:

$$G_i(E_n) = f_i\cdot\sigma_d^{tot}(E_n) \quad .... (6)$$

then,

$$\Delta P_i = t\cdot\int_0^{E_n^{max}} G_i(E_n)\cdot\psi(E_n)dE_n \quad .... (7)$$

whereas,

$$\varphi = \int_0^{E_n^{max}}\psi(E_n)dE_n \quad .... (8)$$

stands for the total flux density ratio of neutron distributed on its energy, so that,

$$\Delta P_i = \varphi\cdot t\frac{\int_0^{E_n^{max}} G_i(E_n)\cdot\psi(E_n)dE_n}{\int_0^{E_n^{max}}\psi(E_n)dE_n} \quad .... (9)$$

However, in our experiment we can get the pure Zr^+ with monoenergy E0, and when En in equation (9) was substituted by E0, then,

$$G_i = \frac{\Delta P_i}{\varphi\cdot t} = \frac{\Delta P_i}{D} \quad .... (10)$$

So the physical meaning of the damage function Gi is revealed clearly, and can be accepted as its definition as follows:

Gi is the increment of the macroproperty index i corresponding to the unit dosage of incident particle, or to each single incident particle.

As shown in equation (3), the linear relation between ΔP_i and Cd is an assumption. if the assumption is not true, then the equations from (4) to (9) would collapse. So it is on the ground of semiexperience. But, when a definition was given to Gi above, the theory get a perfect state. A good parameter Gi which can link corrosion with irradiation and having a clear physical significance.

At the same time, the microstructure change under irradiation was also related to the dose rate[14] which could also be, however, controlled very well in accelerator.

The expression of G with the increment of electrochemical anodic polarization passivation current density

<u>Basic consideration</u>. The consideration is given here of how to endow the concrete meaning of Gi in this experiment. In most engineering situation, materials were used in their passivation state. So that we defined the increment of passivation current density as ΔP_i and the G could be calculated according to equation (10).

<u>The calculation method.</u> The selection of the increment of the passivation current density were conducted according to the steps as follows, 1) found the middle value of potential of the passivation zone of each anodic polarization curve: Emi; 2) calculated the average value of them: $E_b = \frac{1}{n}\sum_{i=1}^{n}(E_{mi})$, where n is the number of the curves; 3) To the same Eb, find the corresponding current density values id of each curve and the corresponding G was calculated using equation (10) and (11):

$$\Delta P = i_d - i_0 \quad\text{..}\quad (11)$$

where id is the anodic passivation current density of the samples irradiated with ions, i0 is that of the unirradiated sample.

<u>The exception.</u> In the case that the average middle potential point falls out of one of the passivation zones, this method becomes invalid.

<u>The built up of G-D function.</u> In order to depict the whole process of irradiation corrosion, the G-D function was built up in this paper by experimental data.

<u>Complementary definition of G when D=0.</u> In the case of unirradiation, D=0, $\Delta P = i_0 - i_0$=0, G=0/0. In mathematics, 0/0 is senseless, but in physics, no irradiation, no damage process. So we define G=0 when D=0 to complete the whole G-D curve.

RESULTS

1. Effect of Zr^+ irradiation on the electrochemical anodic polarization behavior of Zirconium alloy in LiOH water solution at high pressure and high temperature

As shown in Figure 1, with the increase of ion irradiation dose from 0 to 2E15 ions/cm^2, the passivation current density increases. Whereas, as the dose increases to 2E16ions/cm^2, the current density decreases. The parameters ΔP and G were calculated in Table 1. and the G-D curve was given as Figure 2.

2. Effect of Zr^+ irradiation on electrochemical polarization behavior of Zirconium alloy in H_3BO_4 water solution at room temperature

With the same method and parameters (only the temperature and medium are different), the anodic polarization curve and G-D curve were obtained as Figure 3 and Figure 4. With the increment of irradiation dose to 5E15ions/cm^2, the passivation current density dropped and rise again as the dose exceeds this value. The whole G-D curve is kept under G=0 line.

3. Effect of Ar^+ ion irradiation on electrochemical anodic polarization behavior of Zirconium alloy in 1N H_2SO_4 water solution at room temperature

As shown in Figure 5 and Figure 6, the passivation current density decreases as Ar^+ dose grows .The whole G-D curve is under G=0 line. The left half of G-D curve in Figure 6 is similar to that in Figure 4 and the right half of it in Figure 6 is similar to that in Figure 2.

DISCUSSION

Judging from Figure 2 and Figure 3, the anodic passivation current density decreases with increasing ion irradiation dose, i.e. irradiation improved the corrosion resistance of Zirconium alloy; whereas in oxidation experiment in pure oxygen[15, 17], the result is contradictory, the weight gain increased with increasing irradiation dose i.e. the irradiation decayed the corrosion resistance of zirconium alloy; further more, as shown in Figure 1, as the irradiation dose increases the anodic passivation current density increases firstly, and then begin to decrease. It seems that there was not an unifying law of the irradiation corrosion. whether the irradiation corrosion appears as different laws in different corrosion medium?

The answer is no. As shown in Figure 2, Figure 4 and Figure 6 etc.[15], one can see that the G-D curves in different medium are, however, with the same shape basically. No doubt, the irradiation corrosion laws unified on G-D curve.

The proposal of the general theoretical model of irradiation corrosion

On the basis of large quantity of calculations of irradiation effects on electrochemical anodic behaviors of zirconium alloy[15] (Figure 1-Figure 6 are just only a few typical ones), a general theoretical model of irradiation corrosion was electrochemically proposed in Figure 7.

1. The elementary structure of the curve of this model

This model is composed of 3 lines and 11 zones, including 6 linear zones and 5 area zones.

The 3 line: 1) G-O (D=0) line, called the irradiation corrosion starting line, on the left of it, irradiation corrosion never took place, on the right of it, irradiation corrosion takes place definitely; 2) O-D (G=0) line, the zero damage efficiency line, above it, G>0 and the net irradiation corrosion damage efficiency is positive, called the damage zone ; under it,, G<0, the net irradiation corrosion damage efficiency is negative, called the protection zone, means that the samples were not corroded; 3) o-a-b-c-d-e-f line, the irradiation corrosion line which divides the whole process of irradiation corrosion into 6 stages and forms 5 area zones with G=0 and D=0 lines together

The 6 linear zones: 1)o-a, the primary oxidation zone in which a thin oxide film was formed on the surface of the sample during the ion bombardment in vacuum chamber; 2) a-b, the augment zone of the irradiation corrosion damage efficiency, in this zone irradiation corrosion efficiency increases; 3) b-c, the saturation zone of the irradiation corrosion damage efficiency; 4) c-d, the decline zone of the damage efficiency; 5) d-e, the saturation zone of protection effect; 6) e-f, zone of the final decay of the oxide film.

The 6 plane area zones: 1) G>0, the upper half of the whole plane; 2) G<0, the lower half; 3) I-Zone enclosed by o-1-a-1 line, is called the primary oxidation effect zone, the area of this zone has the same dimension as that of ΔP, so that it expresses the total effect of the primary oxidation process on the whole irradiation corrosion; 4) II-Zone, enclosed by 1-b-c-2-1, is called the irradiation corrosion damage zone, the whole area of which expresses the total net irradiation corrosion damage, also with the same dimension as that of ΔP; 5) III-Zone, the area between O-D axis and 2-d-e-f line, is called the

permanent protection zone, in which the thickness of the oxide film on the surface of samples exceeds continuously the whole ion bombardment range.

2. The irradiation corrosion mechanisms involved in this curve

This curve revealed the whole course of the irradiation corrosion of zirconium alloy on the damage efficiency level electrochemically. It included almost all of the stages of the whole life of the materials under irradiation corrosion and included most of the parameters as well as their relations between irradiation and corrosion. At the same time, almost all of the mechanisms of irradiation corrosion were included in this curve.

<u>Effect of oxidation in situ under ion bombardment.</u> On the whole model curve, there reflected a interaction between the oxidation and the irradiation. C. Morant et al[16] stated by calculation that even under 1.33E-6Pa, there existed a monolayer of an absorbed atoms of oxygen. The vacuum degree in our experiments was 1.33E-3Pa. So, the absorbed oxygen existed on the sample surfaces in our experiment. The AES analysis[17] showed that when the Zr^+ dose reached 8E16 ions/cm^2, the thickness of the oxide film increased almost 1 times more than that of the unirradiated one. As shown in Figure 7, at the first stage, the primary oxidation under ion bombardment appears, and at the same stage, the irradiation dose is smaller, so that the protection effect of oxidation subprocess is stronger than that of the irradiation damage and the curve goes down until the lowest point "a" where these two factors got balance.

<u>The mechanism of the enhancement of irradiation corrosion efficiency.</u> As seen in Figure 7, in the second stage (a-b), as the irradiation dose increases and the irradiation corrosion efficiency is enhanced. The damage mechanism dominates this stage. Furthermore a-b can be divided into two substages i.e. a-1 and 1-b, from a to 1, there appears a decrease of the protection efficiency i. e. the decrease of the absolute value of -G, through point 1 where the -G reaches its zero value, the whole process gets into its net damage stage i.e. enters the II-Zone. Hereafter, the irradiation dose and the irradiation effect is stronger enough to overcome the protection effect of the oxidation film until the point 2. Up to now, most literature involved in irradiation corrosion mechanism investigations have been confined within the research of the enhancement of corrosion by irradiation, corresponding to a-b line in this model curve, such as the mechanism of the enhancement of conductivity of oxide film by the change of energy band under irradiation[18], the electric conduction of the precipitates in the oxide films and their decomposition[19], the enhancement of crack of oxide film under irradiation[20] etc.. The basic effect of irradiation is to create a lot of disorder of the lattice atoms in oxide film which changes the shape of the energy band, adding some local conductive states inside the forbidden band along the collision tracts in the oxide films. So that the greater the dose increases, the more severe the disorder forms, the more the conductivity of the oxide film is, the easier the electrochemical corrosion and finally the higher the irradiation corrosion efficiency grows. Naturally, the stage a-b is called the enhancement stage of irradiation corrosion.

<u>The saturation of irradiation corrosion efficiency.</u> In the stage b-c the irradiation corrosion efficiency enters its saturation, which can be related to two aspects. The first is the interaction between oxidation and irradiation, as the irradiation effect and the protection effect of oxidation reaches their new balance point, there would appear a saturation stage. The second is the cascade appeared in the oxide films as the dose increased. When the cascade began, an atom in the collision process might be displaced many times which reflected in the increase of dpa, but finally if this atom disappeared in the defect sink, the net effect equals to one time of displacement. So that under the certain higher dose, the irradiation corrosion efficiency remains steady where the saturation stage appears. In this stage it will produce much error to use dpa to depict the irradiation corrosion.

<u>The decrease of the irradiation corrosion efficiency and reversing into the protection zone.</u> As seen in Figure 7 again, In c-d stage, the irradiation corrosion efficiency decreases and reverses into the protection zone($G<0$) through point "2". The decrease could also be attributed to the two aspects as described in 3.3., when the thickness of the oxide film increased big enough to overpass the irradiation range, the irradiation effect was limited within a surface zone of oxide film and the new born film layer protected the whole

sample from the electrochemical corrosion. But the oxidation process may continue. The thicker the oxidation layer, the lower the curve went down. When the protection effect of oxide film exceeds the damage effect of irradiation, the curve entering the protection zone. Even in the case that the oxide film can not exceed the irradiation range there is also the third explanation of the formation mechanism of this stage i.e. under a very higher dose, the amorphization of the matrix metals or alloys would appear and because that the amorphous metal or alloys can form a passivation film with a very high corrosion resistance on the sample surface, therefore it protected the sample and the curve goes into its protection zone. At point d, where the protection efficiency of the oxide film keeps constant to make the G value on a horizontal level. In stage e-f, with increase of the irradiation dose or if the oxidation film decayed, the curve would rise again and forms its whole "W" shape.

In general, the irradiation efficiency curve is composed of the primary oxidation stage (O-a) , the irradiation enhancement stage(a-b), the saturation stage with constant damage (b-c), the decrease stage (c-d), the protection constant stage (d-e) and the stage of the oxidation film toward decay (e-f).

So that the whole irradiation corrosion course is, in the sense of electrochemistry, not a constant corrosion process but a shift one between the corrosion and protection. The separate stage should be paid more attention in the further study of them.

The relation between the parameters of irradiation and corrosion reflected by the shapes and positions of this model curve

Almost all of the parameters of irradiation and electrochemical anodic polarization as well as the sample materials themselves could be reflected by the variation of positions and shapes of these curves.

The corrosion strength factors of the medium reflected. The corrosion strength factor including the medium, the temperature and the pressure etc. affect not only the shapes of the W-curves but also the positions of them.

Firstly, if the corrosion strength factors were too strong e.g. in the strong H_3NO_3 +HF solution etc., the whole oxidation and irradiation layer would be dissolved chemically as soon as the sample contacted the medium. In this case, the whole W-curve would be eaten by the chemical corrosion and never appears.

Secondly, if the corrosion factors are too weak e.g. in the pure water with room temperature, etc., all of the anodic polarization curves appeared almost all the same and could not be distinguished. In this case, this curve was buried under the and could not be revealed.

Thirdly, as shown in Figure 2, Figure 4 and Figure 6, due to the corrosion factor in Figure 2 is stronger than that in Figure 4 and Figure 6, the I-Zone is eaten by the medium because that the primary oxidation film decayed in the medium of the high temperature and high pressurized water and the II-Zone appears above the G=0 line clearly. However, as shown in Figure 4 and Figure 6, the whole curves appear under the G=0 line, II-Zone are not revealed but I-Zone appears clearly. It means that the medium is too weak.

Fourthly, although the positions of the G-D curves are changed because of the strength of the corrosion factors of the medium, the shapes of the corresponding zones appeared are basically the same such as the enhancement , saturation and decrease zones appeared in the same shapes in Figure 2, Figure 4 and Figure 6, the primary oxidation and enhancement zones appeared in the same shapes in Figure 4 and Figure 6 etc., which reflect that although the medium are various , the basic law of the irradiation corrosion did not change.

So, in general, in the scheme design of the simulation of neutron irradiation corrosion by ion bombardment , this model could be used to optimize the proper medium. If the whole W-curve is under G=0 line which means that the medium and other corrosion strength factors are too weaker and so on.

The control of the irradiation parameters. The slopes of G-D curve reflects the relative comparative relations of the oxidation protection strength factors and that of the irradiation corrosion damage.

Firstly, the better the background vacuum degree in the chamber, the thinner the primary oxide film, and the shorter the length of line o-a or even disappeared. On other hand, the stronger the bombard damage rate of the ions, the shorter the length of line o-a and the longer the line b-c, the longer the line a-b, the smaller the slope of o-a and line c-d, the sharper of the slope of line a-b.

Secondly, the bigger the ion energy and the better the background vacuum was ,then, the longer the line b-c. So line b-c could be used to optimize the ion species and the parameters of irradiation.

The irradiation corrosion resistance of materials. With all of the other parameters fixed, this model curve could be used to compare the irradiation corrosion resistance of different materials. The larger the area of I-Zone, the better the quality of the primarily-formed oxide film; otherwise, the larger the area II (1-b-c-2-1), the worse the irradiation corrosion resistance is; the longer the line d-e, the better the permanent irradiation corrosion resistance is. If there is no a cross point between e-f and O-D, the material, then, seldom to be decayed completely.

3. The unifying of the opinions between experimental investigations and the engineering experiences

The investigations in the laboratories revealed that the enhancement factors of irradiation to the corrosion is between 2 to 10, [8], but the engineering operation of the PWR indicated that the irradiation corrosion resistance of this zirconium alloy cladding is so well that many designers of the PWR neglected the irradiation corrosion. Those two aspects of the irradiation corrosion were unified in this model curve. As shown in Figure 7 again: in the stages o-a-b-c-d the irradiation corrosion is very notable and can not be neglected which is what the experimental scientists emphases, and when the curve entered d-e-f stages the materials entered a steady state of irradiation corrosion which is just the engineering designers emphases. Actually, those two aspects give out the whole irradiation corrosion process of the materials inside the PWR by which the theories and the practice, the experiments and the engineering operation of nuclear materials in PWR during the past half century can be put into one figure and finally get unified.

4. The possible applications of this model curve

To direct the irradiation corrosion experiments, optimum parameters of the simulation experiment such as the ion species, energy, vacuum degree, corrosion medium, pressure and temperature etc.

To evaluate the irradiation corrosion properties of the nuclear materials, direct the research of new nuclear materials, control the irradiation corrosion resistance and quality of the nuclear component on production line, and try to evaluate the service cases inside PWR and other types of nuclear reactors. Although the oxidation was the main process in PWR medium, the electrochemical process was still a company subprocess as the film cracked. Furthermore, the simulation of neutron irradiation by ion bombardment could, at least, be used as a method to evaluate the relative qualities on irradiation corrosion resistance of the nuclear materials.

To create the data base of science and engineering, expand its use to different kinds of reactors and to the irradiation corrosion application in astronautical areas etc.

The data base of the irradiation corrosion properties of materials could be built up on the basis of this theoretical system and on another irradiation oxidation damage efficiency G-D curve[15]. As a ground, the correlation between the neutron irradiation corrosion and the ion irradiation corrosion could be established and the data base of irradiation corrosion in different nuclear reactors and in different environment such as astronautics etc. could be formed and find its new applications in the relative materials research.

Finally, Compared with the E-pH Figure created by Pourbaix and the polarization Figure created by Evans in electrochemistry, the W-curve possesses much more parameters, not only with these of corrosion, but also with those of irradiation, and not only revealed the macrorelations but also the efficiency relations of the whole process of the irradiation corrosion of materials.

The work remained: 1)due to that the number of the experimental points were not big enough, the local shapes of the G-D curves were still waiting to be perfected. 2) the applications of this theory in different reactors under the irradiation of different rays with different energy spectrum would call for a large quantity of concrete research work to be done. But after all, this model presented a key to open the gate of the whole research area.

CONCLUSIONS

1. As a result of the realization of the monovalue of ion energy with accelerators, A parameter G, the irradiation corrosion damage efficiency function was defined theoretically.
2. A G-D function model, a W-shaped curve, was established electrochemically which divided the whole process of ion irradiation corrosion into 6 stages on damage efficiency level i.e. the primary oxidation, irradiation corrosion enhancement, saturation, decrease and reversing into protection zone, protection with constant efficiency and toward the final decay of oxide films.
3. This model curve included almost all of the parameters of irradiation and electrochemical polarization. The variation of the shapes and positions of these curves reflected the special changes of these parameters. This curve involved almost all of the irradiation corrosion mechanisms in its different stages.
4. This model curve unified the contradictory experimental results up to now on the level of irradiation corrosion efficiency electrochemically, and unified the different opinions between experimental investigations and the engineering data and experiences.
5. The applications of model were expected 1) to evaluate the irradiation corrosion resistance of materials, new-invented ones or components on production line in nuclear manufacture plants or in the service in nuclear reactors; 2) to direct the establishment of the date base of irradiation corrosion of different nuclear materials in different reactors and the establishment of the correlation between ion-bombardment-simulation irradiation corrosion and the neutron irradiation corrosion; 3) to help the subjects in other application areas involved in irradiation and corrosion of materials such as the life span estimating and the decay of integrated circuit in spaceflight, etc. 4) to direct the experiments, to coordinate and optimize the relative parameters in the simulation of neutron irradiation corrosion by ion bombardment, such as ion species, ion energies, vacuum degree, corrosion mediums, pressure and temperature etc.

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TABLE 1. Calculation of relative parameters in Figure 1. D(ions/cm^2): the irradiation dose; $R = i_d / i_0, i_d (nA / cm^2)$ and i0: passivation current density; G= ΔP /D, the damage efficiency function indexed with the increment of the anodic passivation current density; ΔP =lgR is the logarithmic increment of anodic passivation current density; the average middle value of potential of passivation zones was taken as Eb=0.88V

D	id	R	ΔP	G
0	2.18E4	1	0	0
2E15	2.29E4	1.05	0.0212	1.05E-17
2E16	1.58E4	0.72	-0.141	-7.15E-18

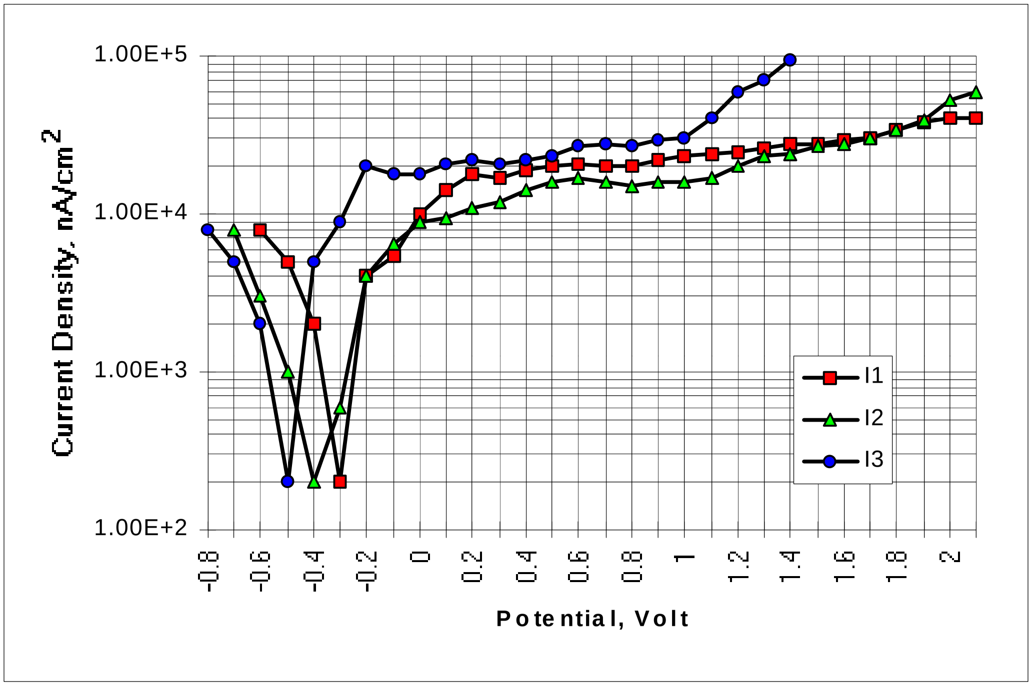

Figure 1 - Effect of Zr+ irradiation on the electrochemical anodic polarization behavior of Zirconium alloy in LiOH water solution at high pressure and high temperature: curve I1, I3 and I2 are with different values of dose of 0, 2E15 and 2E16ions/cm2 respectively with irradiation in liquid nitrogen temperature. The concentration of LiOH in water solution, temperature and pressure are 3.0E-6 Mole, 300 oC and 8.08E6 Pa separately

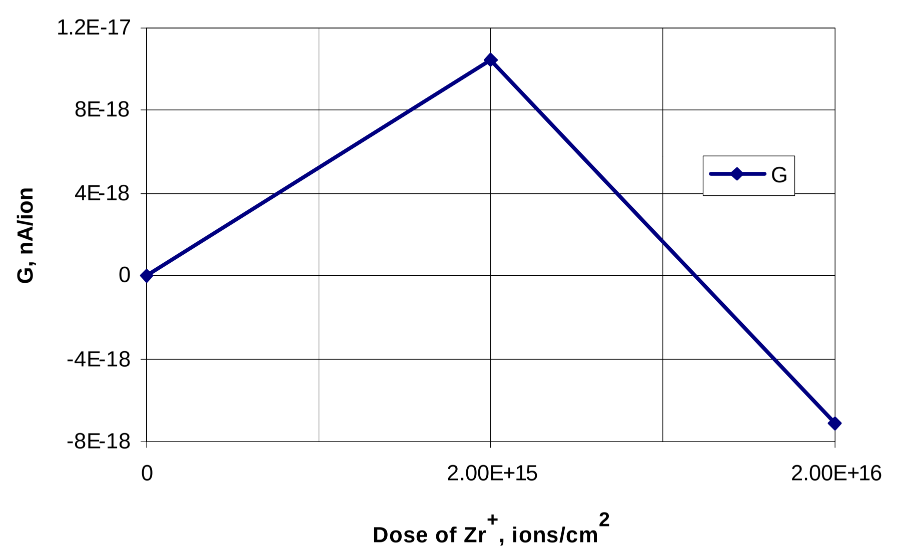

FIGURE 2 - Effect of irradiation dose of Zr^+ on damage efficiency function G indexed with the passivation current density of the zirconium alloy in LiOH water solution at temperature and pressure of 300^{o}C and 8.08E6 Pa individually

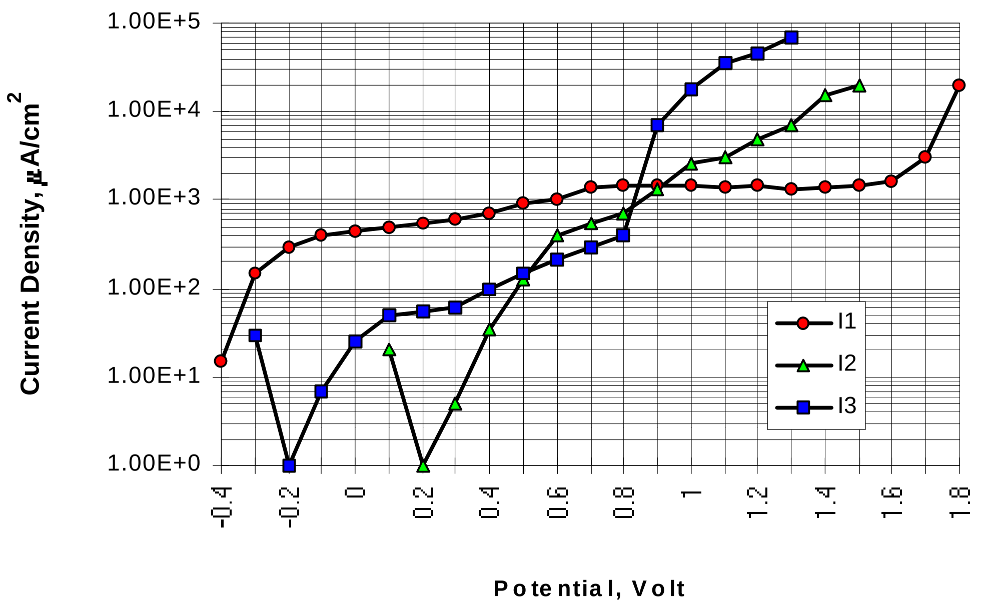

FIGURE 3 - Effect of Zr^+ irradiation on electrochemical anodic polarization behavior of Zirconium alloy in H_3BO_4 water solution at room temperature: irradiation at liquid nitrogen temperature; curve I1, I2 and I3 are with different irradiation doses of 0, 5E15 and 1.9E16 ions/cm^2; the concentration of H_3BO_4 and temperature are 3.0E-6 Mole and 19.3-24.6^{o}C separately.

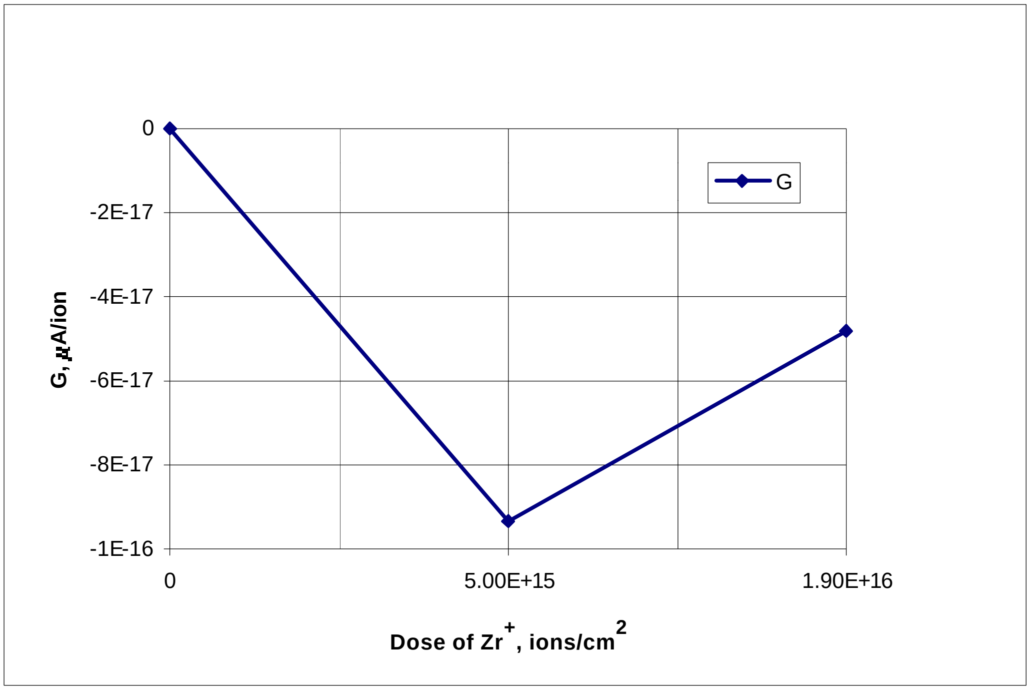

FIGURE 4 - Effect of Zr$^+$ irradiation dose on the damage efficiency function G of zirconium alloy indexed with passivation current density in H_3BO_4 water solution at room temperature.

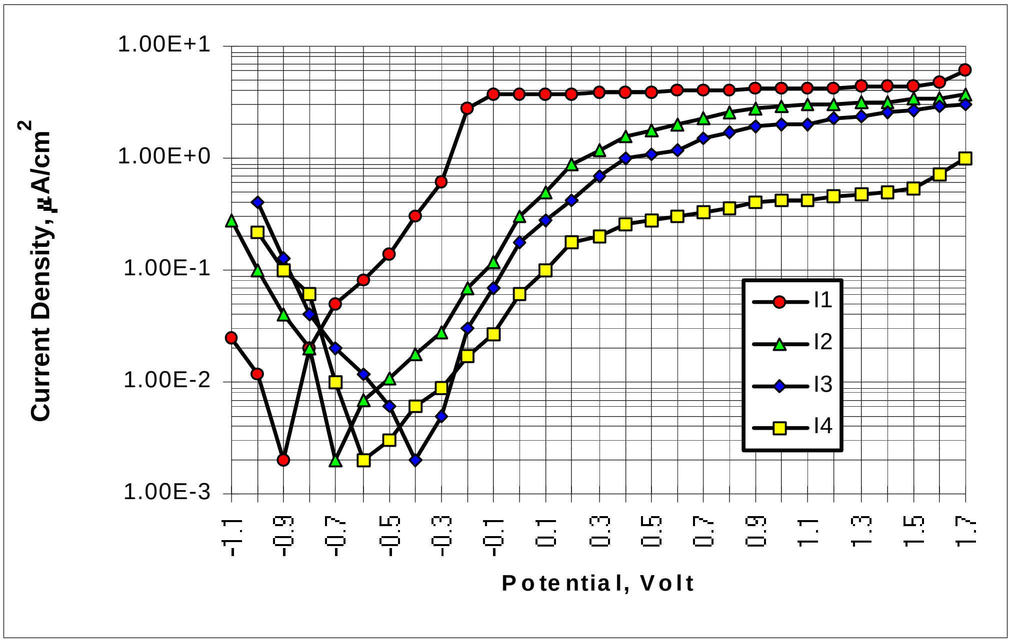

FIGURE 5 - Effect of Ar$^+$ ion irradiation on electrochemical anodic polarization behavior of Zirconium alloy in 1N H_2SO_4 water solution at room temperature: irradiation was conducted at room temperature; curve I1, I2, I3 and I4 are with different irradiation doses of 0, 5E14, 5E15 and 1E16 ions/cm^2 ; the temperature: 19.3-24.6^{o}C

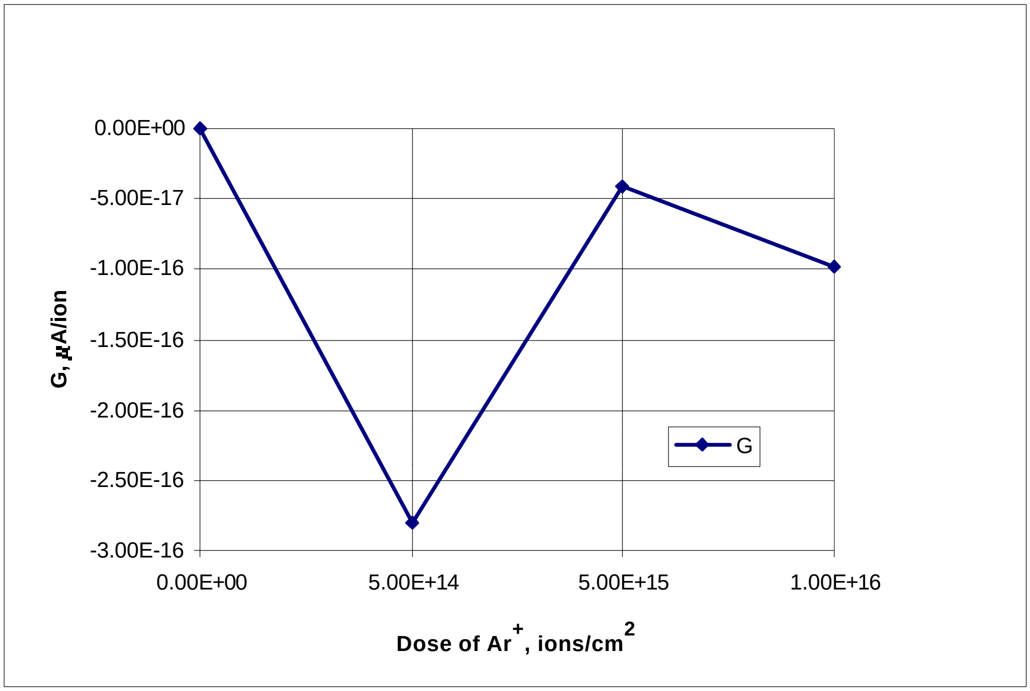

FIGURE 6 - Effect of Ar^+ irradiation on the damage efficiency function G of zirconium alloy indexed with passivation current density in 1N H_2SO_4 water solution at room temperature.

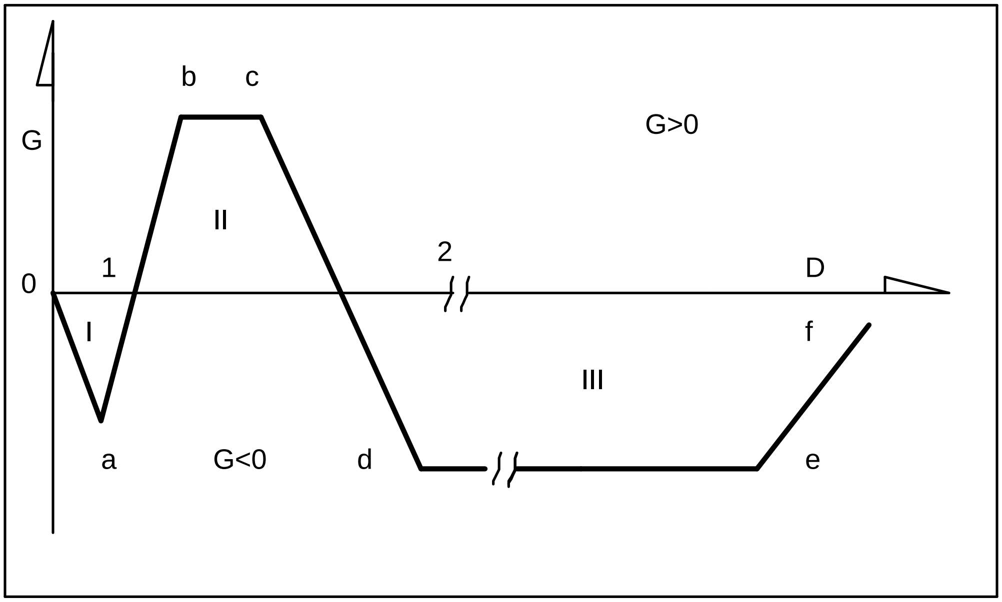

FIGURE 7 - The general theoretical model of irradiation effect on electrochemical anodic polarization behavior: G=0 the zero damage efficiency line; G>0 the damage zone; G<0, the protection zone; o-a, zone of the primary oxidation; a-b, augment zone of the irradiation corrosion; b-c, saturation zone of irradiation corrosion; c-d, zone of the damage efficiency decline; d-e, saturation zone of protection effects; e-f, zone of final decay, 0-G: the beginning line of irradiation corrosion; O-D (G=0) line, the zero damage efficiency line, G>0 the damage zone; G<0, the protection zone.

KEY WORDS:

zirconium alloy, zirconium ion, ion bombardment, irradiation corrosion, electrochemistry, simulation, theoretical model