Lead induced degradation of passive film on Inconel 690 alloy in high temperature and high pressure water

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**Abstract**

Lead has a detrimental effect on Inconel 690 alloy in high temperature and high pressure environment. It is essential to examine how lead influences the corrosion behavior of alloy, and consequently to prevent and control the harmful effects of lead. In this work, the effect of lead on the degradation of Inconel 690 alloy passive film is scrutinized by current sensing atom force microscopy (CSAFM), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The first principle calculations are performed to investigate the effect of lead on band gap and oxygen vacancy energy of passive film. On the whole, lead can combine with metal cation vacancy into the passive film, and promote dehydration process of Cr(OH)3 while inhibit Ni(OH)2 dehydration, resulting in the reduction of spinel oxides and the increase of hydroxides in the passive film. In addition, lead can enter into the oxide layer and blocks the outward diffusion of oxygen vacancies, which reduces the oxygen content in the passive film finally. The coupling of the lead effects on dehydration and vacancy diffusion changes chemical structures and electronic properties of the passive film, accelerates the corrosion rate and causes the degradation of the passive film. These findings provide physical insights in the degradation mechanisms of the passive film on Inconel 690 alloy.

1. **Introduction**

Nuclear Power as a clean, stable and economic energy has been developing for more than 60 years, which has obvious advantages in solving the energy crisis and improving the environmental quality. Thus, nuclear power has been developing vigorously in many countries, and accounts for a considerable proportion of the world's total electric power. However, there are some vital issues to remain to resolve. Many structural materials in nuclear power plant may be failure due to suffer from aggressive environments for a long time, which will cause a lot of economic losses. Many researches have been made to explore their failure mechanisms, aiming to improve protective measures and extend the service time of the material.

Heat transfer tube made of alloy 690 is a key component for connecting the primary circuit and the second circuit in pressurized water reactors (PWR). There are many ways for lead to enter into the secondary side, such as plant makeup water, condenser cooling, copper alloys in condensers and feed-water heaters. Even only 0.1 ppm lead may cause Pb-assisted stress corrosion cracking (PbSCC) of the heat transfer tube in high temperature and high pressure environment [1]. The fracture morphology of PbSCC for 690TT alloy can be both transgranular and intergranular [2-3]. It has been found that the presence of lead can induce the SCC mode of such alloy altering from intergranular to transgranular around grain boundary carbides [4]. According to Zhang et al’s work, lead not only exists at the crack paths, but also exists in the passive film [5]. Despite the current understanding of lead effect, the mechanism of PbSCC is still controversial. When the concentration of lead in solution as well as the contents of M-OH and M-OH2 bonds in the passive film increase, the rupture ductility of the passive film decreases. The lower rupture ductility the passive film, the higher SCC susceptibility the alloy 800 in lead-contaminated environments [6]. Hence, understanding the influence of lead on the passive film is the key to PbSCC in nickel-based alloys.

Levite et al. [7] and Machet et al. [8] have reported that the passive film of nickel-base alloys consists of multilayer structure in primary simulated medium, including a continuous internal layer of Ni(1-x)FexCr2O4 or Cr2O3, an external layer of nickel hydroxide, and nickel ferrite heterogeneously dispersed on the surface. Passive film of 690 alloy formed in alkaline environment at high-temperature also showes a similar structure [9]. Kim et al. [10] has observed that passive film of 600 alloy showes a porous outer layer and a continuous internal layer in an alkaline solution, but only showes a single oxide layer in a lead contained solution. The role of lead in corrosion processes of 690 alloy is strongly dependent on the pH value of the testing solutions. In acidic environments the effect of lead on corrosion process is almost negligible, while in neutral and alkaline environments lead brings big impact to anodic dissolution and film modification [11]. In the latter case, lead will participate in the forming process of passive film by altering the passive film structure, hindering hydroxide dehydration process and retarding the formation of spinel oxides. This induces the hydroxide contents increase and the protective spinel oxides decrease, and ultimately the property of the passive film degrades. The presence of lead-contaminant promotes the entry of other dissolved species, such as hydrogen in alkaline media and calcium [11-14]. Moreover, it has been reported that lead or calcium individually has detrimental effects on nickel base alloy in crevice solutions, and there is also a coupling effect that calcium can mitigate the detrimental impact of lead on nickel base alloy when calcium and lead are both in crevice solution [15-16].

In the present work, the degradation mechanism of 690 alloy by lead is explored by using pure water with 1 ppm lead as the solution. Surface morphology and the chemical component of the passive film are characterized by using scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. Localized electrical behaviors are analyzed by current sensing atom force microscopy (CSAFM). The effect of lead on film band gap and oxygen vacancy were performed by the first principle calculations. The possible degradation mechanism due to the ingression of lead is discussed according to the experimental results.

**2. Experimental methods**

*2.1. Material and sample preparation*

The nickel-based tubing material UNS N0690 alloy was used as the test material, which’s composition in weight percent was 30Cr, 10Fe, 0.5Mn, 0.5Si, 0.02C, and bal. Ni. The tube was 5 mm long and 19 mm outer diameter with 1.08 mm wall thickness. The samples were wet ground with SiC paper up to #5000, mechanically polished using 1 μm diamond paste, and then electrochemically polished in a mixed solution of HNO3:CH3OH=3:7 for 30s at an applied voltage of 1.5V. The process ensured that the surface stress layer was removed and the grain boundary could be distinguished from the grain interior. Finally all samples were cleaned in ethanol and de-ionized water, and dried with air.

Samples were pre-passivated at 270$°C$ and 5.2~5.7 bar for 168h at open circuit potential in pure water without and with 1ppm lead. The purpose was to compare the behavior of passive film formed without and with lead in aqueous solutions in neutral pH. Before passivation, the solution was deaerated using 4~5 MPa high-purity Argon for 1 h at room temperature. After passivation, specimens were cleaned in ethanol and de-ionized water, and dried with air.

*2.2. Current sensing atom force microscopy (CSAFM) measurement*

The CSAFM measurement was conducted using an Agilent 5500 system. A copper wire was drawn from the side of the sample and connected to the system as the bottom electrode, and the probe acted as a top electrode over the sample. System parameters were all the same for the measurements, and the probe used was the same. The probe was conductive Pt-coated silicon tip, which’s sensitivity coefficient was 35 nm/N and elastic constant was 1 N/m. Deflection was 1.75 volt. Tip bias was 2 volt. The scanning area was all $10×10 μm$.

*2.3. X-ray Photoelectron Spectroscopy*

All XPS measurements were characterized using a PHI Quantera SXM produced by ULVAC-PHI company. Photoelectron from Al target was emitted with an incident angle of 45 degrees relative to the sample surface. The spectra were obtained at step size 0.1eV with 55eV pass energy. Analysis chamber vacuum was better than 10-7 Torr. The C1s peak at 284.8eV was used as the standard to correct the energy shifts. Depth profiling was conducted over X ray beam spot with a diameter of 100 $μm$ under Ar-ion sputtering, and the sputter rate was 17nm/min based on calibration using a thermal oxidation SiO2.

*2.4. First principle calculations*

The first principles calculations, which was based on Density Functional Theory (DFT) within the local density approximation LDA+U [17]and the projector augmented wave (PAW) pseudo-potential [18], were implemented in the Vienna Ab-initio Simulation Package (VASP) [19]. All calculations were performed with the plane-wave cutoff energy of 400 eV. For the Brillouin-zone integrals, Monkhorst-Pack scheme [20] on the basis of the 3×3×1 *k*-point mesh was used. The Gaussian smearing method with the smearing width of 0.05 was employed to describe the total energy. With regard to structural relaxation, all the atoms were allowed to relax until force on each atom was less than 0.01 eV/ Å. The most common Cr2O3 crystal was hexagonal corundum structure (space group R-3c), and the following crystal lattice parameters were used in the calculations, a = b = 4.958 Å, c = 13.59 Å, *α* = *β* = 90°, *γ* = 120° [21]. For transition metal Cr, an effective on-site Coulomb repulsion U was introduced to describe the strong intra-atomic electronic correlations in Cr2O3 [22-23]. The U parameter of Coulomb repulsion was tested by fitting to experimental band gap. The band structure proved that when the U parameter was 5.5 eV, the band gap of bulk *α*-Cr2O3 material was 3.37 eV in theory. This result was consistent with the experimental value 3.4 eV [24]. Consequently, 5.5 eV was taken as the U parameter in the calculations. A 2×2×1 Cr2O3 thin film was built as shown in Fig. 1a, and a vacuum layer of 15 Å was considered to eliminate the coupling effect of neighboring slabs along the [001] direction. A chromium atom in 2×2×1 Cr2O3 thin film was substituted by a lead atom to investigate the effect of lead on band gap and oxygen vacancy energy.

**3. Results**

*3.1. The effect of lead on the passive film morphology*

The surface morphology of the obtained passive film has been observed by scanning electron microscopy, as shown in Fig. 2. In the lead-free sample, the passive film consists of a compact crystalline structure and some scattered particles in the outmost layer. However, only adding 1 ppm lead to pure water, passive film becomes loose and porous, and no clear crystalline structure is observed. The change in the passive film structures induced by lead is similar to Kim’s work in which sodium hydroxide solutions are used [10].

*3.2. The effect of lead on the element concentration of the passive film*

The element atomic concentration in the passive film have been measurement by XPS, and the comparison of lead with lead-free results is plotted in Fig.3. It can be seen that a chromium-rich outmost layer always forms, regardless of the presence of lead or not. The relative diffusion rates between nickel, chromium and iron in the oxides are different. Nickel and iron diffuse more rapidly than chromium [9], so nickel and iron quickly dissolve but hardly deposit. Chromium diffuses slowly and combines with oxygen and hydroxyl. Therefore, there is only the chromium-rich layer observed in the passive film. Moreover, the presence of lead increases the atomic ratio of nickel, iron and chromium while decreases oxygen in the passive film. This suggests that lead can hinder the outward diffusion of nickel, chromium and iron, as well as the transport of oxygen into the inner. The thickness corresponding to half of the surface oxygen concentration is defined as the thickness of the passive film [25]. Thus, the thickness of the passive film in lead-containing and lead-free solutions are 18.5nm and 9.2nm, respectively.

The profiles of oxide and hydroxide of nickel and chromium are plotted in Fig.4. For oxides, lead will decrease the relative contents of both chromium and nickel oxides compared with lead-free samples. For hydroxides, it is reduced for chromium, but increased for nickel with the addition of lead. Nevertheless, the total relative content of hydroxyl in passive film formed in containing-lead aqueous solution is increased. The decrease in relative contents of protective chromium and nickel oxides by lead causes the passive film less protective [26-27].

The element atomic concentration of lead in the passive film is shown in Fig. 5a. The atomic ratio of lead is 0.93 atomic percent at the distance 2.5 nm from surface an-d reduces to about 0.1 atomic percent at about 32 nm depth. That is to say, lead not o-nly alters the component and structure, but also participates in the formation process of the passive film. The detailed XPS spectrum of passive film for lead element at the distance 5 nm from surface can be obtained, and lead exits mainly in the form of lead hydroxide and metallic lead, as shown in Fig. 5b. The generation of metallic lead may come from the replacement reaction between lead hydroxide and metallic nickel [13]:

$Pb\left(OH\right)\_{2}+Ni \rightarrow Pb+Ni(OH)\_{2} ∆G\_{300℃}= -43.9kJ/mol$ (1)

However, it is too low for the intensity of XPS spectrum at the place beyond 5 nm from the surface of the passive film that the existence form of lead is unclear from XPS results, due to only 1 ppm lead added in the solution. When adding several hundred or ten thousand ppm lead into caustic solution, lead oxide was found in the passive film of alloy 600 [10, 28]. Therefore, it’s very reasonable that there will be lead oxide at the place beneath 5 nm from the surface of the passive film.

*3.3. Localized electrical behaviors of passive film*

The electrical behavior of the passive film has been characterized by CSAFM, a-nd the effect of lead on the topography and electrical property is identified, as shown in Fig. 6. When adding 1 ppm lead into pure water at 270$°C$ and 5.2~5.7 bar, changes on the surface topography and its current feature of the passive film is pronounced. S-imilar to the SEM images in Fig. 2, the quantities of scattered particles on the outerm-ost surface of lead-contained passive film (Fig. 6c) decrease significantly compared with a lead-free passive film (Fig.6a). In lead-free passive film, current signal can be seen only around scattered particles on the outermost surface. In contrast, with additi-on of lead, a current peak is detected on both sides of grain boundary and the current value of grain interior increases apparently. These phenomena indicate that lead will result in a sharp increase of defects in the both sides of grain boundary and grain interior according to Souier T’s work [29].

Passive film is acted as semiconductor film [30-31], which can be characterized by electrical resistivity *ρ*:

$ρ=VA ⁄ Id$ (2)

where $V$ is tip bias and $I$ is average current over a certain area. Here area *α* and *β* in grain interior in Fig.6 b and d is calculated by Agilent processing software. *d* is the passive film thickness. $A$ is contact area between tip and sample which can be calculated by equation (3):

$A = πa^{2} = π(3PR ⁄ 4E^{\*})^{2 ⁄ 3 }$ (3)

where *P* is the applied force and equals to between deflection, sensitivity and elastic constant. *R* is the tip radius of 30 OEsystem+alculated as rateides will retard the outward diffusion of metal cations, whichns from metal atoms, nm. $E^{\*}$ is the effective young’s modulus of the tip and the sample and defined as $E^{\*}=\left[{(1-υ\_{1}^{2})}/{E\_{1}+}{(1-υ\_{2}^{2})}/{E\_{2}}\right]^{-1}$, in which $υ\_{1}$,$ υ\_{2}$, and $E\_{1}$, $E\_{2}$ represent the Poisson’s ratio and young’s modulus of the tip and the sample, respectively. The following values are used, $υ\_{1}= 0.28$, $E\_{1}= 169GPa$, $υ\_{2}= 0.285$, $E\_{2}= 190GPa$ [32-33]. Finally, electrical resistivity can be obtained and the results are shown in Table 1. With only 1ppm lead, electrical resistivity of passive film in grain interior drastically decreases about 142 times. The electrical property of passive film in grain interior is seriously degraded.

*3.4. The effect of lead on band gap and oxygen vacancy formation energy in Cr2O3 film*

The energy band structure diagrams are shown in Fig. 7. Energy at 0 eV corresponds to the Fermi level. Band gap for the 2×2×1 Cr2O3 thin film is 2.228 eV, and reduces to 0.407 eV with only a chromium atom substituted by a lead atom. Thus, it is obvious that electrons are more easily excited in the 2×2×1 Cr2O3 thin film containing a lead atom.

When an oxygen atom with different distance from lead atom is taken away, the total energy can be obtained by the first principle calculations shown in Table 2. The formation energy of oxygen vacancy, *EV*, can be calculated as:

*EV* = *E – ES* + *EO*

where *ES* is the calculated system total energy of 2×2×1 Cr2O3 thin film containing a lead atom. *E* is the total energy of lead-containing system with an oxygen atom missed. *EO* represents the energy of an oxygen atom. *E* can be used for comparing the vacancy formation energy, as *ES* and *EO* are the same for oxygen vacancies I, II, III and IV. For oxygen vacancies I, II and III, the closer oxygen vacancy to lead atom, the lower the formation energy. That is to say, oxygen vacancy tends to cling to lead atom. Compared with oxygen vacancies I, II and III, the formation energy of oxygen vacancy IV where is on the surface of thin film is the lowest. Hence, oxygen vacancies tend to diffuse to the surface of thin film, which is consistent with the point defect model [34].

**4. Discussion**

*4.1. Ingression of lead-contamination*

Lead may exist in two ionic statuses in the solution and degrade the film property via the corresponding mechanisms. On the basis of potential-pH diagram [35], lead would exist stably in the form of PbOH+ in neutral solution. Taking the polar model into account, the passive film consists of an inner anion-selective layer and an outer cation-selective layer [36]. The excess oxygen ions and metal cation vacancies at outer layer can provide fixed negative ionic charge. Hence, PbOH+ will easily be absorbed on the surface of passive film, and then form hydroxide with $OH^{-}$:

$PbOH^{+}+OH^{-}\rightarrow Pb(OH)\_{2}$ (4)

According to the point defect model developed by Macdonald et al [34]. PbOH+ may occupy metallic cation vacancies and enter the passive film via the vacancy diff-usion mechanism.

  (5)

  (6)

  (7)

  (8)

There may also exist Pb2+ produced by the dissociation of PbOH+, and Pb2+ can get into the passive film in the same way with PbOH+ [12]. Finally, two types of lead ion both participate in the formation process of passive film, and change the electronic structure and chemical structure of passive film.

A chromium-rich passive film always forms regardless of the presence of lead or not, as mentioned in section 3.2. Therefore, the passive films are mainly composed of chromium hydroxide and oxide, and oxides in the passive film are mainly Cr2O3 and NiO•Cr2O3 on the basis of XPS results. According to the point defect model (PDM), cation vacancies generated at the film/solution interface diffuse in the oxides to the film/metal interface [34]. Pb2+ can occupy cation vacancies at film**/**solution interface by equations (7) and (8), and enter the oxide layer via the vacancy diffusion mechanism [12, 34]. In addition, there may be another way for lead into oxide layer. Pb(OH)2 and Cr(OH)3 dehydrate gradually to form PbO•Cr2O3. In fact, the spinel oxides in the passive film are nonstoichiometric, in order to facilitate analysis using stoichiometric compounds.

*4.2. Structure changes of passive film induced by lead*

During passivation process, hydrogen atoms can diffuse into metal atom gap and trap electrons from metal atoms, which weaken metal atomic bond. As a result, atomic O and OH could easily move inside metal surfaces and form a passive film, which consists of oxides and hydroxides [37-39]. Previous works [11-16, 36] have demonstrated that hydroxides can gradually transform into oxides by the process of dehydration, resulting in that more oxides would form in the passive film. Thermodynamic calculations have shown that spinel oxides are very stable, and the solubility of spinel oxide is extremely low [26]. These properties of spinel oxides will retard the outward diffusion of metal cations, which decreases the corrosion rate of metal in high temperature [27].

It is expected that the more stable hydroxide, the more difficult the dehydration process. From the viewpoint of thermodynamics, the stability of hydroxides can be evaluated with equilibrium constants for the dehydration reactions. The equilibrium constants for dehydration of Cr(OH)3 , Pb(OH)2 and Ni(OH)2 at 270$°C $are shown in Table 3. The stability of hydroxides obeys the following order: Cr(OH)3 < Pb(OH)2 < Ni(OH)2. Thus, lead can accelerate the dehydration process of Cr(OH)3 and hinder the dehydration process of Ni(OH)2 ,which results in the decrease of Cr(OH)3 (Fig. 4b) and the increase of Ni(OH)2 (Fig. 4d). However, the relative content of Cr(OH)3 reduces, and the relative content of chromium oxides doesn’t increase. This is associated with the reduction of oxygen in passive film (Fig. 3). Finally, passive film contains more hydroxide (Fig. 4e) and less oxide with the presence of lead, resulting in that the properties of passive film degrade.

The element atomic concentration of oxygen in the passive film is shown in Fig. 3f. It is found that the atomic concentration of oxygen in the passive film reduces when adding 1 ppm lead into solution. According to the point defect model [34], oxygen vacancies transfer from the metal/film interface to the film/solution interface in the oxides, and oxygen ion combines with oxygen vacancies at the film/solution interface entering the passive film by vacancy diffusion mechanism. Basing on the first principle calculations in section 3.4, the formation energy of oxygen vacancies where are nearest-neighbor and next-nearest-neighbor of lead atoms is lower than that of other oxygen vacancies, except for that of oxygen vacancies on the surface of the passive film. Hence, when oxygen vacancies diffuse near lead atoms, part of oxygen vacancies will occupy oxygen vacancy locations at the nearest-neighbor and next-nearest-neighbor of lead atoms and are pinned at these positions. Then, other oxygen vacancies cannot pass through these positions and will bypass these positions as shown in Fig. 8. Therefore, lead atoms impede the outward diffusion of oxygen vacancies, and block the growth of passive film finally.

*4.3. Electrical properties changes of passive film induced by lead*

When adding 1ppm lead into high temperature and high pressure water, electrical resistivity of passive film in grain interior drastically decreases about 142 times. The electrical property of passive film in grain interior is seriously degraded, which is related to the structure and composition changes of passive film. On the one hand, passive film with and without lead are chromium-rich layer, and lead reduces the relative content of Cr(OH)3 and Cr2O3 in the passive film. When lead drops Cr2O3, the band gap decreases from 2.228 eV to 0.407 eV according to section 3.4. On the other hand, the relative content of Ni(OH)2 increases, and the relative content of nickel oxides which is manly NiO decreases. The band gap of Ni(OH)2 (3.15 eV) is less than that of NiO (3.66 eV) [40-41]. The narrower the band gap is, the easier the electrons escape. Hence, electrical resistivity of passive film with lead in grain interior drastically decreases. Corrosion usually is an electrochemical process, accompanied by electron transfer. When electrical resistivity of passive film is reduced, the electron transport capacity of the passive film is enhanced. Therefore, the tendency of corrosion will increase, and alloy corrosion rate is accelerated in lead-contaminated environments.

**5. Conclusions**

CSAFM, XPS and SEM are used to study the influence mechanism of lead on 690 TT alloy in high temperature and high pressure water. XPS, SEM and the first principle calculations reveal the detrimental effect of lead on the structure and composition. Micro region electrical properties is degradation due to lead, which can be detected by CSAFM. The following new views can be drawn:

1. Lead hinders the dehydration process of nickel hydroxide but promotes the dehydration process of chromium. Finally, the content of spinel oxides is reduced, and the overall proportion of hydroxides increases. The lead-containing passive film is degradation.
2. Lead can enter the oxide layer in the passive film, and hinders the outward diffusion of oxygen vacancies. Therefore, the oxygen content that can enter the passive film decreases, and the growth of passive film is blocked by lead.
3. Lead can cause the degradation of electronic properties. Electrical resistivity of passive film in grain interior decreases near 142 times. The material is more susceptible to corrosion.

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