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Nano-Channels Early Formation Investigation on Stainless Steel 316Ti after Immersion in Molten Pb-Bi

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Abstract

Development of fuel cladding and structural materials in Pb-Bi environment, especially at high temperature, is a critical issue for the deployment of LFR (Lead alloy-cooled Fast Reactor) and ADS (Accelerator Driven Transmutation System). This is because of the corrosive characteristic of Pb-Bi to metals as constituent materials of fuel cladding and structural of the reactors. Corrosion test of a high-chromium austenitic stainless steel i.e. SS316Ti in molten Pb-Bi at 550 °C has been carried out for about 300 hours continuously. The characterization using SEM-EDS (Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy) showed that an iron oxide as the outer layer and a chromium oxide as the inner layer on the surface of the specimen were formed which in general have protected the steel specimen from corrosion and dissolution attack of Pb-Bi. However, small amount of Pb could penetrate into the iron oxide layer through ultra-narrow channels. Atomic Force Microscopy (AFM) with Electrostatic Force Microscopy (EFM) mode was employed to investigate the phenomena of the nano-channels early formation. The results of the nano-scale investigation showed clearly the formation of the channels at the early time of corrosion as the way of Pb to penetrate into iron oxide outer layer.

Abstrak

Investigasi Pembentukan Awal Saluran-Nano pada Baja SS316Ti Setelah Pembenaman di Cairan Pb-Bi
Pengembangan material kelongsong bahan bakar dan struktur reaktor nuklir di lingkungan Pb-Bi terutama pada temperatur tinggi merupakan isu penting bagi penyiapan LFR (reaktor cepat berpendingin paduan timbal) dan ADS (sistem transmudasi yang digerakkan oleh akselerator). Hal ini karena karakteristik korosif Pb-Bi pada logam bahan penyusun dari kelongsong bahan bakar dan struktur reaktor. Pengujian korosi baja austenitik kromium tinggi yaitu SS316Ti dalam cairan Pb-Bi pada temperatur 550 °C telah dilakukan selama sekitar 300 jam secara kontinu. Hasil analisis SEM-EDS (*Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy*) menunjukkan bahwa oksida besi sebagai lapisan luar dan oksida kromium sebagai lapisan dalam pada permukaan spesimen telah terbentuk yang secara umum melindungi spesimen baja dari korosi dan serangan disolusi Pb-Bi. Namun, sejumlah kecil Pb dapat menembus ke dalam lapisan oksida besi melalui saluran ultra-celah sempit. *Atomic Force Microscopy* (AFM) dengan mode EFM (*Electrostatic Force Microscopy*) telah digunakan untuk menyelidiki fenomena pembentukan awal saluran tersebut. Hasil penyelidikan skala nano menunjukkan dengan jelas pembentukan saluran tersebut pada saat awal proses korosi yang menjadi jalan bagi Pb untuk menembus lapisan luar oksida besi.

Keywords: Nano-channel, Pb-Bi, corrosion, SS316Ti, AFM

1. Introduction

LFR (Lead alloy-cooled Fast Reactor) with lead-bismuth (Pb-Bi) eutectic (LBE) as a coolant is one of the future nuclear reactors in the world (Generation IV reactors) [1-5]. Liquid Pb-Bi eutectic is also a spallation

target material and a coolant for ADS (Accelerator Driven Transmutation System) [1-3]. However, the development of LFR and ADS meets with the corrosive characteristic of liquid Pb-Bi eutectic to metals especially iron, nickel and chromium as constituent materials of fuel cladding and structural of the reactors [6-21].

Therefore, one of the key issues for the deployment of LFR and ADS is the development of high corrosion resistant materials for the fuel cladding and structural materials in liquid Pb-Bi eutectic environment especially at high temperature.

Many types of materials have been developed in many countries to overcome the issue i.e. steels, ceramics, refractory metals, and coated steels [6-21]. Up to now, steels are the most candidates for fuel cladding and structural materials of LFR and ADS. One of them is a high chromium austenitic stainless steel type of SS316 [8,10-14,16,20-21]. It has been expected that protective oxide layers which are formed on the surface of the steels because of oxygen concentration controlling could protect the steels from corrosion attack of Pb-Bi. However, it was reported that ferritization phenomena occurred because of Ni and Cr dissolution into the Pb-Bi for JPCA stainless steel after tested in liquid Pb-Bi eutectic at 450 °C of temperature for 1,000 hours and oxygen concentration of $\sim 10^{-8}$ wt.% [8]. For long-term corrosion test in liquid Pb-Bi eutectic, it was reported that local dissolution attack increases with exposure time and can reach a depth of 400 μm for SS316L after tested for 10,000 h at temperature of 550 °C and oxygen concentration of 10^{-6} wt.% [10]. Nevertheless, up to now, the scientific reports of early-corrosion and dissolution attack behavior of Pb-Bi for 316 stainless steel type are limited. Moreover, reports on nano-scale penetration of Pb-Bi into SS316 are more limited. Therefore, the purpose of present study is to investigate in nano-scale characterization the early-corrosion attack behavior of Pb-Bi which form nano-channels formation for 316 stainless steel type after immersion in liquid Pb-Bi eutectic at 550 °C of temperature for several hundred hours.

2. Experiment

The corrosion test has been carried out using COSTA facility at Institute for Pulsed Power and Microwave Technology-Karlsruhe Institute of Technology Germany as shown in Figures 1. The experiment has been reported [12]. The test specimen was an SS316Ti with the chemical composition is shown in Table 1.

The test sample was placed inside a crucible made of ceramic that has already filled of liquid Pb-Bi eutectic. The crucible then placed inside the reaction tube of corrosion test apparatus made of quartz. Gas mixture of Ar and Ar +5% H₂ gases were flowed into water tubes to produce steam then injected continuously to the reaction tube during corrosion test. Control of the oxygen concentration in the liquid Pb-Bi eutectic was done by adjusting the partial pressure of p_{H₂}/p_{H₂O}. An oxygen sensor was placed for measuring oxygen concentration during corrosion test by monitoring the

generated EMF (electromotive force) in voltage scale. The test sample of SS316Ti was immersed in the liquid Pb-Bi eutectic at 550 °C of temperature for about 300 hours with 10^{-6} wt.% of the oxygen concentration.

The characterizations of the tested sample were done using SEM-EDS (Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy) for morphology, micro structure, and element analysis. Afterward, Atomic Force Microscopy (AFM) with Electrostatic Force Microscopy

Table 1. Chemical Composition of SS316Ti (wt.%)

Fe	Cr	Ni	Mo	Ti	C
Balance	16.5-18.5	10.5-13.5	2.0-2.5	0.70	0.08

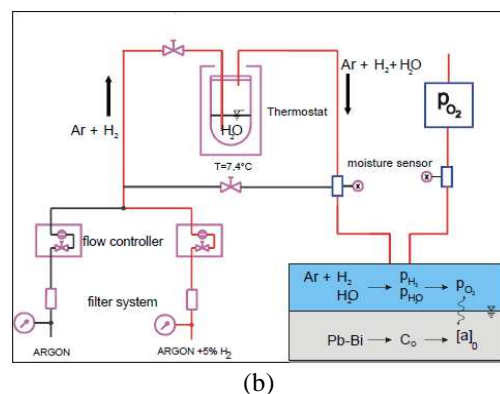
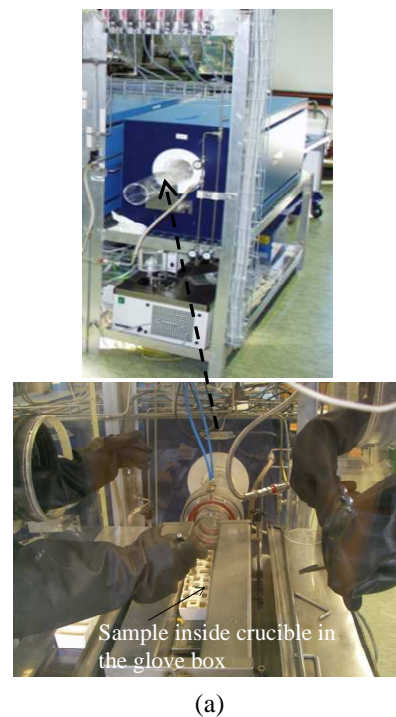
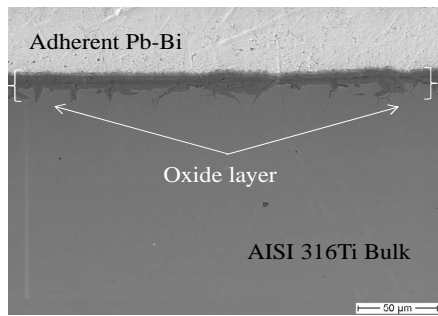
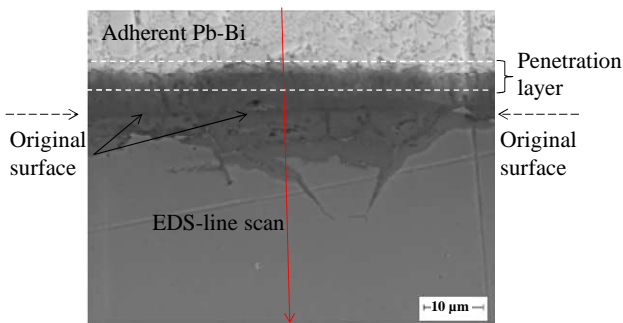


Figure 1. Corrosion Test Apparatus COSTA (a) Corrosion Test and Glove Box System (b) Schematic of Oxygen Control System



(a)



(b)

Figure 2. SEM Micrograph of the Cross Section of the Samples (a) 200 Times of Magnification (b) 2,000 Times of Magnification

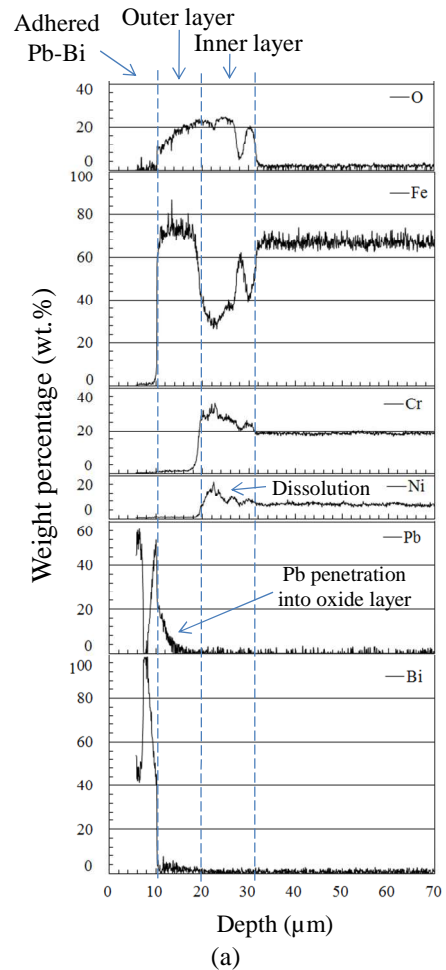
at Center For Science and Technology of Advanced Materials BATAN was employed to investigate the nano-channels formation.

3. Results and Discussion

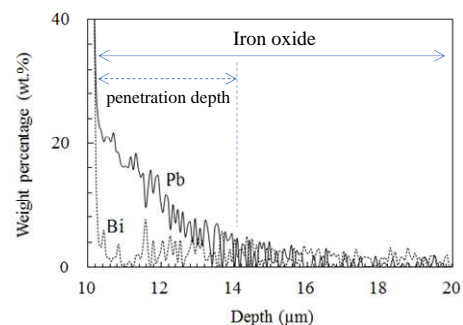
SEM analysis for the sample cross section after immersion in molten Pb-Bi is shown in Figure 2(a) for 200 times of magnification and 2(b) for 2,000 times of magnification. The general results have been reported [12]. Figure 2(a) shows the formation of oxide scale on the SS 316Ti. The oxide scale form is typical for the whole of the area. Figure 2(b) shows that the oxide scale was a duplex layer. The thickness of the duplex layer was about 15 μm, i.e. ~5-6 μm for outer layer and ~5-9 μm for inner layer. It can be observed that underneath of the inner layer some of oxygen diffusion traces which formed of oxide layer was indicated. The analysis revealed that the original surface of the sample was in the middle of the duplex layer as shown in Figure 2(b).

EDS analysis for the sample cross section after immersion in molten Pb-Bi which the line scan is indicated in Fig. 2(b) is shown in Figure 3(a) for O, Fe, Cr, Ni, Pb, Bi elements analysis and (b) for Pb, Bi, Fe elements analysis. The EDS analysis results showed that iron oxide was formed as the outer layer and iron-chromium oxide was formed as the inner layer. The results also

showed the dissolution direction of nickel from the bulk to the Pb-Bi but it was detained by the inner layer. Furthermore, the trace of Pb penetration into the outer layer was observed as shown in Figure 3(b). However, there was no penetration of Pb and Bi atoms into the inner iron-chromium oxide layer and the matrix of the specimen underneath of the iron-chromium oxide layer. The inner layer could withstand from the corrosion and dissolution attack of Pb-Bi for about 300 hours.



(a)



(b)

Figure 3. EDS Analysis with the Line Scan is Indicated in Fig. 1(b) of the Cross Section of the Samples (a) O, Fe, Cr, Ni, Pb, Bi Elements (b) Pb, Bi, Fe Elements

Penetration of Pb into the outer layer should be through the ultra-narrow channels because it could not be observed clearly in the microscopic scale. Therefore, nano-scale investigation to analyze the early formation of the ultra-narrow channels because of corrosion attack of Pb-Bi is needed. In order to analyze the phenomena of nano-scale formation of the Pb penetration therefore Atomic Force Microscopy with electrostatic force microscopy (EFM) mode was employed. The EFM mode was EFM external with non-contact mode.

Figures 4 and Figures 5 show the AFM analyses for topography profile in 2 dimensions, electrostatic force in 2 dimensions, and merger between topography and

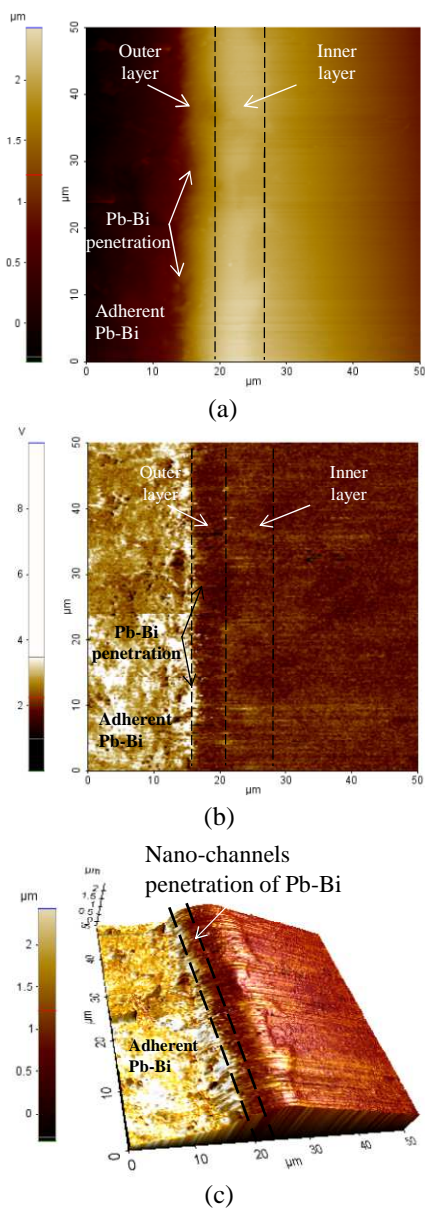


Figure 4. AFM Analysis of the Cross Section of the Samples with the Area 50x50 μm (a) Topography Analysis (b) EFM Analysis (c) Combination EFM-topography Analysis in 3D

electrostatic force profiles in 3 dimensions. Figures 4 show the AFM analyses for 50x50 μm scale area to observe the whole area of the duplex oxide layer i.e. outer layer and inner layer on the surface of SS316Ti and Figures 5 show the AFM analyses for 5x5 μm scale area to observe the penetration of Pb into the surface of the iron oxide outer layer.

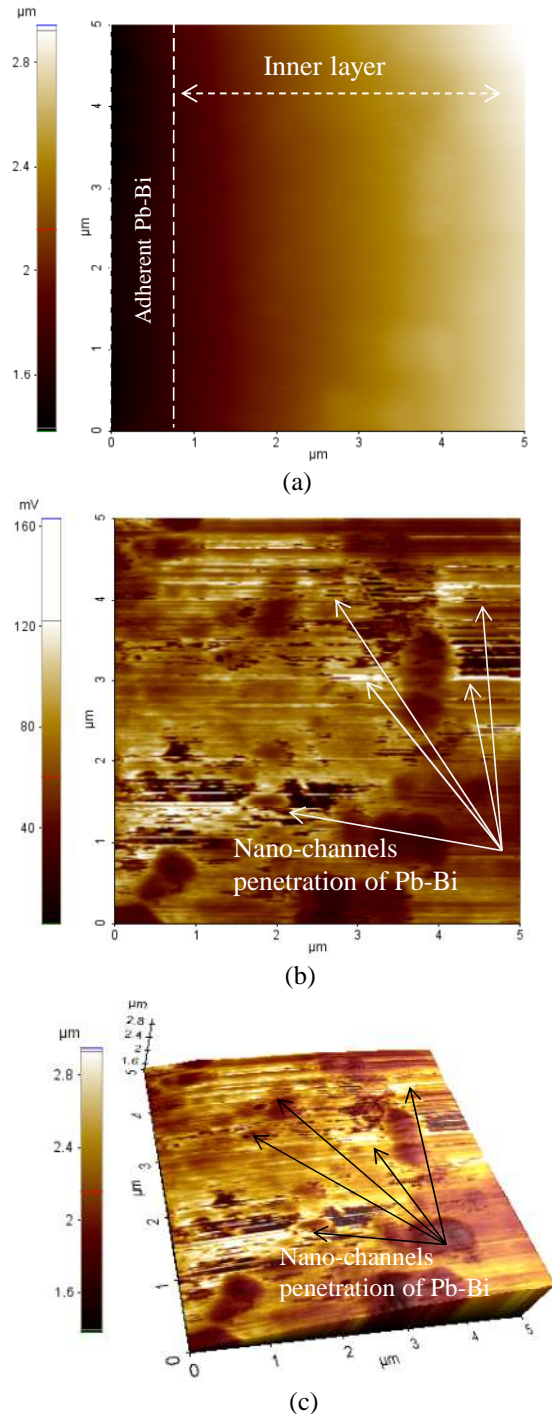


Figure 5. AFM Analysis of the Cross Section of the Samples with the Area 5x5 μm (a) Topography Analysis (b) EFM Analysis (c) Combination EFM-topography Analysis in 3D

The Van der Waals forces between the tip of AFM cantilever and the sample surface were measured and the magnitude of these forces change according to the tip sample distance was used to measure the surface topography. The sample surface properties i.e. the interaction force of the electrostatic force between the EFM biased tip and sample was observed to measure the electrical properties of the surface. Each material has different electrostatic force interaction therefore it is able to distinguish among different materials.

Figure 4(a) shows the topography for the whole area of the duplex oxide layer with outer layer and inner layer. It could be analyzed that the surface of the area was smooth therefore the Van der Waals forces between the tip and the sample surface did not interfere the electrostatic force between the EFM biased tip and sample. Figure 4(b) shows the electrostatic force of the whole of the duplex oxide layer area with outer layer and inner layer. It could be analyzed that the electrostatic force interaction was different for each area. Furthermore, the Pb-Bi electrostatic force properties were higher compared with other areas. Therefore, it is able to observe the presence of Pb-Bi from the electrostatic force scale. Figure 4(c) shows the merger between topography and electrostatic measurement in 3 dimensions in order to observe the sample in more details. It was found clearly the area of outer-layer, inner-layer, adherent Pb-Bi and also penetration area of Pb-Bi into the surface of outer-layer. However, the penetration area of Pb-Bi into the surface of outer layer was still disturbed by the adherent Pb-Bi area. Therefore, smaller and focused area for ultra-narrow penetration Pb-Bi is needed.

Figure 5(a) shows the topography of the iron oxide area outer layer. It was expected that the penetration of Pb-Bi through ultra-narrow channels could be observed. The surface of the area was smooth therefore the Van der Waals forces between the tip and the sample surface did not interfere the electrostatic force between the EFM biased tip and sample. Figure 5(b) shows the electrostatic force of the similar area with Figure 5(b) i.e. iron oxide area as the outer layer. Various electrostatic force scales were observed. It could be analyzed that there was highest electrostatic force area revealed. From the previous EFM analysis as shown in Figure 4(b) it could be predicted that the highest electrostatic force was belong to Pb-Bi. Moreover, from the EDS analysis it can be analyzed that the penetration was done by Pb atoms as shown in Figure 3(b). Therefore, the highest electrostatic area as shown in Figure 5(b) was Pb penetration area. Furthermore, the area of Pb penetration was in the ultra-narrow channels formation. Figure 5 (c) shows the merger between topography and electrostatic force measurement in 3 dimensions in order to observe the sample in more details. It was found clearly the area of ultra-narrow penetration area of Pb-Bi into the the

outer layer. The ultra-narrow penetration of Pb was in the hundreds and tens nano-meter of channel diameter, therefore it is so-called nano-channels.

The corrosion mechanism of SS316 has been reported by others researchers [17]. A lot of researches have been carried out to protect SS316 from corrosion attack of Pb-Bi such as surface modification or alloying using intense pulsed electron beam [20] and aluminum-alloy coating on the steel [21]. In order to understand the corrosion phenomena in details, ultra-narrow penetration of Pb-Bi into the steel has been predicted theoretically [19] and reported for different case [18] by other researchers. The present study revealed the phenomenon of early nano-channels formation of Pb penetration into SS316Ti after immersion in Pb-Bi at 550 °C for about 300 hours.

4. Conclusion

The corrosion test of a SS316Ti austenitic steel in liquid Pb-Bi at 550 °C of temperature and 10×10^{-6} wt.% of oxygen concentration for about 300 hours has been done. Penetration of Pb into the iron oxide outer layer was observed. The penetration was very narrow and formed nano-channels on the iron oxide outer layer. AFM with EFM mode is able to investigate the formation of the nano-channels. It is able to be understood that the corrosion attack of Pb-Bi to the steel in the early process started from nano-channels penetration.

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