STAGNANT Pb-Bi CORROSION EXPERIMENT FOR HYPER MATERIALS*

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Abstract

HYPER (HYbrid Power Extraction Reactor) is the accelerator-driven transmutation system developed by KAERI (Korea Atomic Energy Research Institute). HYPER is designed to transmute long-lived transuranic actinides and fission products such as ^{99}Tc and ^{129}I. HYPER adopts a fast neutron system and Pb-Bi is used as core coolant and target material. Pb-Bi corrosion is one of the main factors considered to set the upper limits of temperature and velocity. Therefore, KAERI planned Pb-Bi corrosion experiments, and a stagnant Pb-Bi corrosion experiment was performed for HYPER structure materials as the first step. The experiment was performed under the oxygen-controlled atmosphere.

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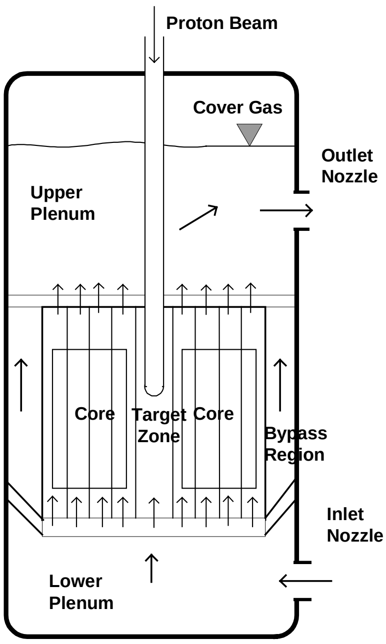
Introduction

HYPER (*HY*brid *P*ower *E*xtraction *R*eactor) is the accelerator-driven transmutation system which is being developed by KAERI (Korea Atomic Energy Research Institute). [1] An accelerator-driven system can reduce plutonium, minor actinides, and environmentally hazardous fission products from the nuclear waste coming from the conventional nuclear power plant. In addition, it can be used to produce electricity. HYPER is designed to transmute TRU and fission products such as ^{99}Tc and ^{129}I. Figure 1 shows the outline of HYPER.

Figure 1. **The outline of HYPER**



HYPER uses Pb-Bi as the coolant and target material which is not separated. One of the main problems due to Pb-Bi is corrosion. It was shown that corrosion attack happened into about 100 µm deep region from the surface for ferritic steels under the condition of 575-750°C and 3 250 h of exposure. [2]

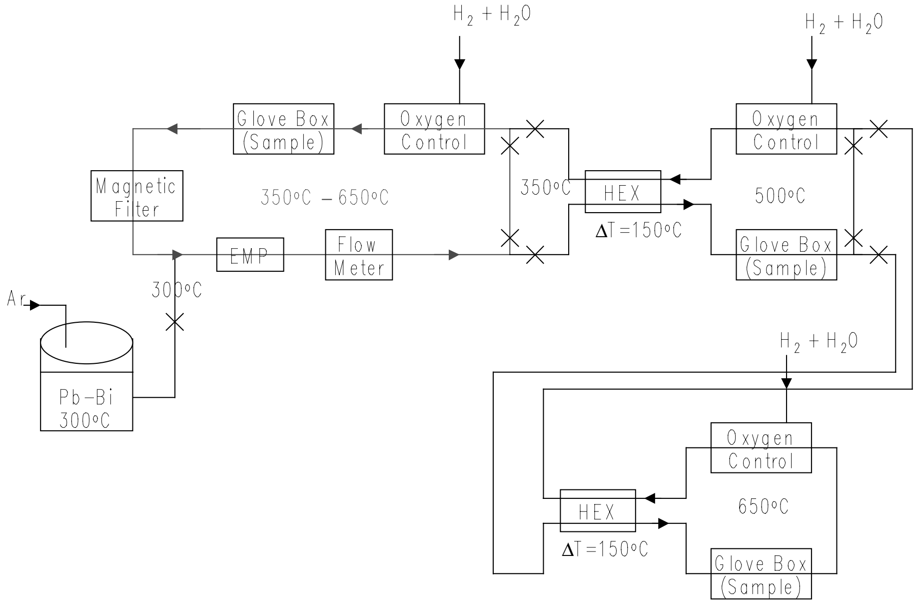
The inlet temperature of Pb-Bi is designed to be 340°C for HYPER. The average outlet temperature is 510°C. The maximum temperature exists at the cladding surface, which is about 650°C. The candidate cladding materials are 12Cr steels such as HT-9. Therefore, we should find out the conditions of preventing Pb-Bi corrosion at 650°C. One method is to form a stable oxide layer on the material through oxygen control in Pb-Bi. Another one is to modify material compositions or the surface of material. If we can not find out an appropriate method to prevent corrosion, the design should be modified so that the maximum temperature decreases.

We consider 9Cr steels such as T91 and 9Cr-2WVTa as the candidate beam window materials. The maximum temperature of the beam window contacted with Pb-Bi is designed not to exceed 500°C. In case of the beam window, Pb-Bi corrosion effect can be combined with the radiation damage to produce more severe damage.

KAERI's plan for Pb-Bi corrosion study

KAERI has a plan to build a Pb-Bi loop for corrosion study. The design of Pb-Bi corrosion loop is being progressed. Figure 2 is the outline of the KAERI Pb-Bi loop.

Figure 2. **The schematic drawing of KAERI Pb-Bi loop**



The main characteristic of KAERI loop is to investigate samples at 3 different temperatures at the same time. Since the Pb-Bi temperature range of HYPER is 340-650°C, KAERI loop is designed to have 350, 500, 650°C temperature zones. The oxygen content is controlled by one of 3 control systems located at different temperature regions to study the controllability of oxygen content at each temperature zone. Oxygen control is performed by flowing Ar/H_2 gas mixed with H_2O vapor. The maximum available velocity of Pb-Bi will be 2 m/s.

The design of the loop will be finished in 2002. The construction will start in 2003. Once the first isothermal loop is built, we will start running the loop and testing materials while building additional second and third isothermal loops. At the same time, a stagnant Pb-Bi corrosion test facility will be built.

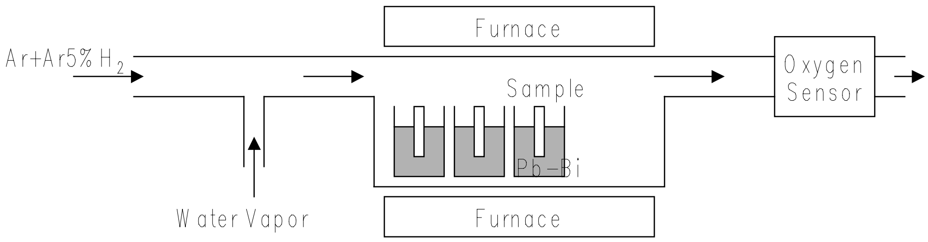
We also have a long-term plan to build a proton irradiation test loop. KAERI launched KOMAC project which is to build a high power proton accelerator. The first stage of KOMAC project is to build 100MeV, 20mA proton linac by 2012. Once the proton beam is available, we can make a Pb-Bi loop which includes test samples irradiated by proton beams. In that way, we can investigate the combined effect of Pb-Bi corrosion and radiation damage on samples. That kind of investigation is necessary for the beam window materials.

Until KAERI has its own corrosion test facilities, we will use foreign institute's facilities for the test of HYPER materials. As the first step, we have been using FZK's stagnant corrosion test facility, COSTA. [3] In this paper, we show the first result of the experiment performed by using COSTA.

Experiment procedure

Figure 3 shows the layout of FZK's Pb-Bi corrosion test facility. Al_2O_3 crucibles are filled with Pb-Bi and heated to a certain temperature. Three different temperatures are chosen to cover the HYPER temperature range. They are 350, 500 and 650°C. Each crucible contains 32 g of Pb-Bi. The experiment was performed with three different oxygen contents, which are $<10^{-8}$wt% (reduced), 10^{-6}wt% and 10^{-5}wt%. When a reduced atmosphere is needed, Ar5%H_2 gas is forced to flow with the rate of 35 cm^3/sec for 3 days. Then samples are put into the Pb-Bi for corrosion test. The oxygen content in the gas was measured by an oxygen partial pressure meter throughout the experiment.

Figure 3. **Schematic layout of the FZK stagnant corrosion test facility COSTA**



Ar, Ar5%H_2 and H_2O vapor are mixed to produce 10^{-6} and 10^{-5}wt% oxygen contents. Equation 1 is used to calculate the corresponding oxygen partial pressure. [3] Then Equation 2 is used to determine the pressure ratio of H_2 and H_2O. The H_2O pressure is set to be 15.94mbar. Ar gas is forced to flow with the rate of 100 cm^3/sec and the corresponding rate of Ar5%H_2 gas is also forced to flow.

$$\frac{C}{C_S} = \left(\frac{P_{O_2}}{P_{O_{2,S}}}\right)^{\frac{1}{2}} \qquad (1)$$

$$P_{O_2} = \frac{{P_{H_2O}}^2}{{P_{H_2}}^2}\exp\left(\frac{2\Delta G_{H_2O}}{RT}\right) \qquad (2)$$

where C_S is the solubility of oxygen in Pb-Bi.

Six different kinds of samples were selected for the corrosion test. Table 1 shows the components constituting each sample. HT-9 is the candidate material of HYPER fuel cladding. HT-9M and HT-9MN are modified HT-9. They are developed by KAERI. 9Cr-2WVTa is the candidate material of HYPER beam window. 9Cr-1Mo is another 9Cr steel and 316LN is an austenitic steel.

Table 1. **Components of samples** (atomic %)

	C	Si	Mn	Ni	Cr	Mo	V	Nb	W	P	S	N
9Cr-1Mo	0.099	0.32	0.42	0.10	9.03	0.96	0.22	0.094	–	<0.003	0.003	0.032
HT9M	0.145	0.1	0.45	0.46	9.79	1.23	0.2	0.18	–	<0.003	<0.003	0.02
HT9MN	0.15	0.072	0.49	0.50	10.0	1.28	0.205	0.204	–	0.002	0.004	>0.02
HT9	0.19	0.36	0.59	0.53	11.79	0.99	0.31	0.02	0.49	0.019	0.006	<0.01
316LN	0.022	0.53	0.87	10.6	17.69	2.61	–	–	–	0.02	0.001	>316SS
9Cr-2WVTa	0.11	0.21	0.44	<0.01	8.90	0.01	0.23	–	2.01	0.015	0.008	0.0215

The samples are 2 mm thick and the heat treatment was done at 1 050°C for 1 hour and 750°C for 2 hours except 9Cr-2WVTa. In case of 9Cr-2WVTa, the heat treatment was done at 1 050°C for 15 minutes and 750°C for 1 hour.

Results and discussion

The motivation of the stagnant corrosion experiment is to investigate the degree of corrosion damage for HYPER materials due to the dissolution by stagnant Pb-Bi. The first step should be the investigation of corrosion due to pure Pb-Bi, where oxygen potentials lower than that of Fe_3O_4 are used. If a material is not damaged by pure Pb-Bi under the working temperature range of HYPER, we can conclude that the material can be used without considering the effect of corrosion. For example, the thickness of HYPER fuel cladding is designed to be 0.68 mm and the lifetime of the cladding should be at least 3 years. The safety criterion on the cladding is that no more than 10% of the cladding thickness should be damaged. That means about 23 μm/y is the limit for the damage of the cladding.

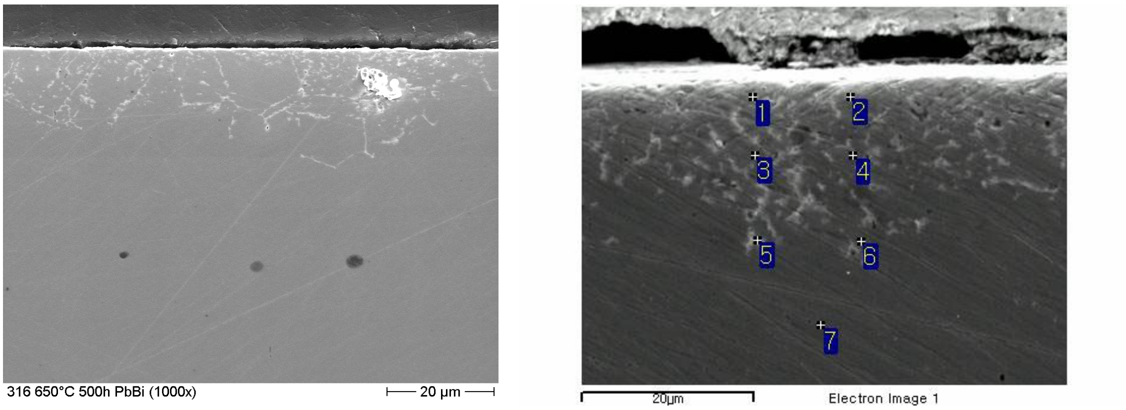
If there is a severe corrosion damage to affect the stability of the structure made of a material, the next step is to invent a method to prevent corrosion based on the test results of pure Pb-Bi corrosion. One of known methods of preventing corrosion is to put a specific material such as oxygen into Pb-Bi. Other methods are the surface modification, development of new materials and combinations of more than two methods. In this study, we used only the oxygen control method for the prevention of corrosion. The maximum exposure time is 2 000 hours for the stagnant experiment. We cut the samples at 500 and 1 000 hours to investigate them. If we see the severe damage from 500 or 1 000 hours old samples, we stop the test. Therefore, materials can be screened by the stagnant test.

Once a material turns out to be stable under stagnant test, the next step is to study the corrosion damage due to the flowing Pb-Bi. If materials pass the flowing Pb-Bi test, the final stage is to check the effects of radiation damage and impurities in the material and Pb-Bi. Impurities are produced by nuclear reactions due to neutrons and protons. If we can not find any material or a surface modification method which is stable under corrosion attack at a certain temperature, we should decrease the design temperature.

The stagnant experiment of six materials has been progressed and is still being performed. In this paper, we focus on the corrosion of HT-9 and 316LN at the temperature of 650°C. Figure 4 and 5 shows SEM results of 316LN and HT-9 exposed to Pb-Bi with reduced oxygen for 500 h respectively.

The oxygen meter shows that the oxygen content in the flowing gas is less than 10^{-27} bar, which means the oxygen content in the Pb-Bi is less than 10^{-8}wt%. Dissolution attack is clear for the 316LN sample and the corrosion pattern is homogeneous through the sample surface. The maximum depth of dissolution is about 40μm. EDX analysis was done for a part of the sample. Table 2 shows the atomic % of main elements of the sample, Pb, Bi and O for each point of investigation.

Figure 4. **SEM results of 316LN sample with reduced oxygen**



Point 7 in Figure 4 is located inside the sample, so it is not affected by Pb-Bi corrosion. Points 1 and 2 are located just below the surface and there is no Ni content in those regions. It was observed that more Ni and Cr are dissolved in the white region where Pb and Bi penetrate into the sample. Ni has a higher tendency to be dissolved than Cr. Bi has a higher tendency of penetration than Pb. That is due to the different solubilities of the components. The solubility of Fe, Cr and Ni are 12.1, 23.4 and 36 700 ppm respectively at 600°C Pb-Bi. [4] A small amount of oxygen is detected at point 1, the source of which is not quite clear yet. It should not happen if the oxygen reduction is perfect.

Figure 5. **SEM results of HT-9 with reduced oxygen**

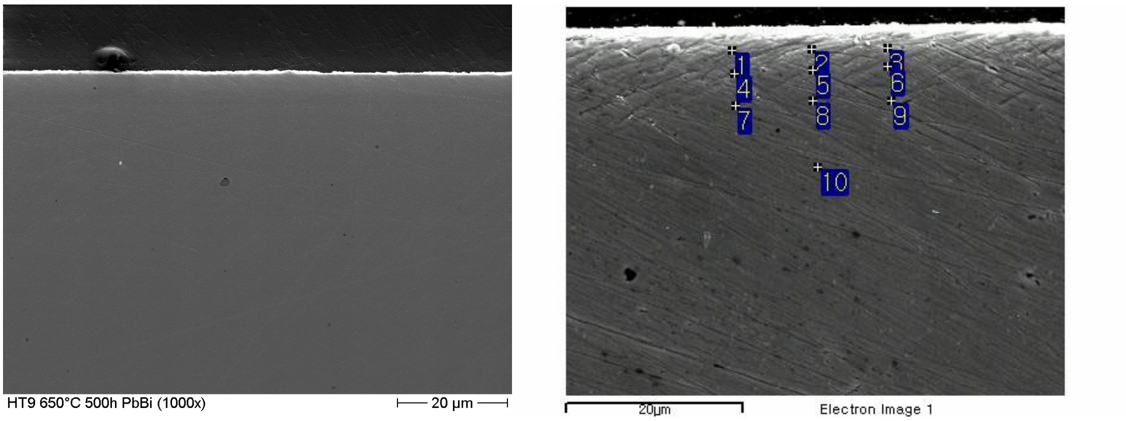


Table 2. **EDX results of 316LN at points described in Figure 4** (at. %)

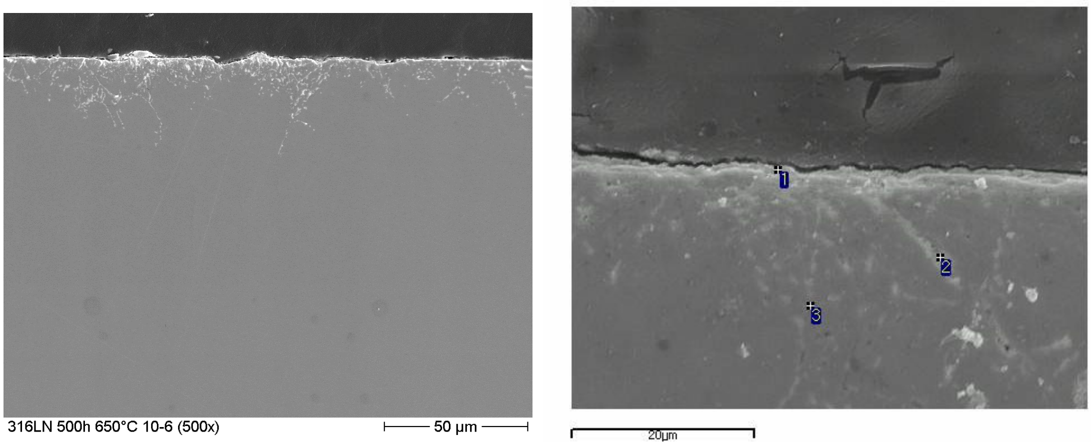
	Fe	**Cr**	**Ni**	**Pb**	**Bi**	**O**
1	52	19			21	8
2	73	27				
3	70	20	9		1	
4	69	18	11		2	
5	73	19	8			
6	78	15	2	2	3	
7	69	20	11			
Original	70	19	11			

Table 3. **EDX results of HT-9 at points described in Figure 5** (at. %)

	Fe	Cr	Pb	Bi	O
1-3	88.4	11.6			
4-6	86.1	13.9			
7-9	86.0	14.0			
10	86.4	13.6			
Original	87.8	12.2			

In case of HT-9, no clear corrosion attack was seen for the 500 h sample. Figure 5 shows the clean surface of HT-9. EDX analysis was also performed, and Table 3 lists the average atomic % of Fe and Cr for 3 points located at the same depth level. It shows that Cr is dissolved near the surface, but the dissolution is not large compared to 316LN. HT-9 and 316LN samples are still being exposed to 650°C Pb-Bi with reduced oxygen content and we will investigate 1 000 h and 2 000 h samples. Although we are investigating the corrosion at 650°C with a reduced atmosphere, it is generally known that the corrosion of steels is severe at 650°C and the corrosion protection is needed. Therefore we also investigated the corrosion at 650°C with controlled oxygen. Figure 6 and 7 are SEM pictures of 316LN and HT-9 exposed for 500 h with 10^{-6}wt% of oxygen.

Figure 6. **SEM results of 316LN with 10-6wt% of oxygen**



In case of 316LN, a stable oxide layer was not formed with 10^{-6}wt% of oxygen. The corrosion pattern is similar to the case of reduced atmosphere. The difference between reduced atmosphere case and 10^{-6}wt% case is that a high oxygen atomic % is detected at some regions of sample surface and regions attacked by Pb-Bi. Table 4 shows the atomic % of the main elements at points described by numbers in Figure 6. We can see that an oxide layer is formed at point 1, but the layer is not firm enough to prevent the corrosion. There is Pb-Bi penetration at point 2.

Table 4. **EDX results of 316LN at points described in Figure 6** (at. %)

	Fe	Cr	Ni	Pb	Bi	O
1	30	8		9		53
2	59	11		2	10	18
3	87	13				

As can be seen in Figure 7, HT-9 of 10^{-6}wt% case shows much different characteristics from the case of reduced Pb-Bi. When the oxygen content is 10^{-6}wt%, the corrosion is severe and the pattern is inhomogeneous. Figure 7(a) is the pattern which can be seen most frequently. But there are some regions attacked deeply by Pb-Bi, which are shown in Figure 7(b). The largest depth is about 120 µm and most of Cr is depleted in that region. On the contrary, there are some regions where an oxide layer is formed and no Pb-Bi attack appears. Figure 7(d) is one of such regions. We are investigating the reason of severe corrosion with oxygen content of 10^{-6}wt% compared to the case of reduced Pb-Bi.

Figure 7. **SEM results of HT-9 with 10-6wt% of oxygen**

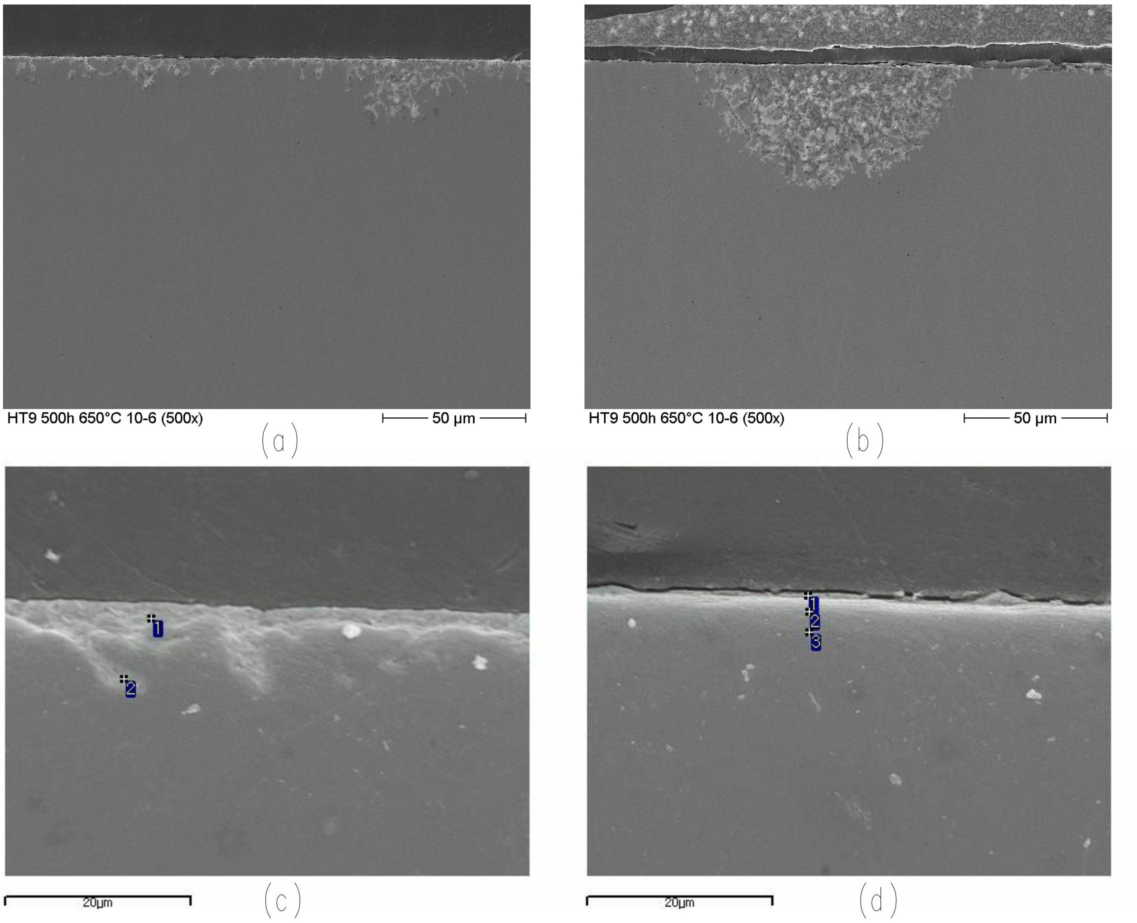


Table 5. **EDX results of HT-9 at points described in Figure 7** (at. %)

	Fe	Cr	Pb	Bi	O
(c) 1	98	2			
(c) 2	42	2	11	10	35
(d) 1	50	10	3		37
(d) 2	80	10			10
(d) 3	88	12			

Summary

KAERI plans to build a Pb-Bi loop for corrosion study. The design of Pb-Bi loop is being progressed and it will be finished in 2002. The construction will start in 2003. At the same time, a stagnant Pb-Bi corrosion test facility will be built. We also have a long-term plan to build a proton irradiation test loop. Until KAERI has its own corrosion test facilities, we will use test facilities operated by foreign institutes. As the first step, we used FZK's stagnant corrosion test facility. Three different temperatures are chosen to cover the HYPER temperature range. They are 350, 500 and 650°C. The experiment was performed with three different oxygen contents, which are $<10^{-8}$wt% (reduced), 10^{-6} wt% and 10^{-5}wt%. Six different kinds of samples were selected for the corrosion test. They are HT-9, HT-9M, HT-9MN, 9Cr-2WVTa, 9Cr-1Mo and 316LN. The maximum exposure time is 2 000 hours for the stagnant experiment. In this paper, we focused on the corrosion of HT-9 and 316LN exposed for 500 h at the temperature of 650°C with a reduced atmosphere and 10^{-6}wt% of oxygen. When the test was performed with a reduced atmosphere, dissolution attack was clear for the 316LN sample. The maximum depth of dissolution is about 40 μm. Although the oxygen content is changed to 10^{-6} wt%, the corrosion also happened. In case of HT-9, we did not see the clear corrosion attack with a reduced atmosphere. But a severe corrosion happened when the oxygen content is changed to 10^{-6} wt%. We are investigating the reason of difference between the corrosion of a reduced atmosphere case and that of 10^{-6}wt% case for HT-9.

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