High temperature corrosion of cold worked YUS409D bellows of bellow-sealed valve in LBE

A P A Mustari1*, D Irwanto1 and M Takahashi2

1Nuclear Physics and Biophysics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Ganesha Street No 10, Bandung 40132, Indonesia

2Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, N1-18, 2-12-1 O-okayama, Meguro-ku, Tokyo, 152-8550, Japan

*E-mail: pramutadi@fi.itb.ac.id

Abstract. Lead-bismuth eutectic (LBE) loop test is highly contributes to the lead-alloy-cooled fast breeder reactor (LFR) and accelerator driven system (ADS) research and development by providing comprehensive results of both corrosion and erosion phenomenon. Bellows-sealed valve is a crucial part in the LBE loop test apparatus, due to its capability of preventing corrosion on valve spring, thus improves the operation time of the system. LBE is very corrosive to stainless steel by formation of oxide layer or elemental dissolution, e.g. Ni. Thus, new type of bellows for bellows-sealed valve made of nickel free material, i.e. YUS409D, is proposed to be used in the LBE. Bellows material undergo heat treatments for mechanical improvement including cold working and annealing. The thickness reduction by the heat treatments is about 90% of initial condition. Corrosion behavior of the bellows has been studied in stagnant LBE at 500 and 600 °C for 500 hours. The oxygen concentration was controlled at about $10^{-7}$ wt%. Typical oxide layers were developed on the surface. Oxidation rate was sharply increased at 600°C.

1. Introduction

Lead-bismuth eutectic (LBE) is a candidate material for coolant of the lead-alloy-cooled fast breeder reactor (LFR) and, for target and coolant of accelerator driven system (ADS) due to its advantageous. However, LBE is very corrosive to the structural material at high temperature. It is a better condition for ADS, i.e. MYRRHA project, in comparison with LFR since the proposal temperature of the cooling will be set below 450°C. For the fabrication the utilization of material treatments, e.g. annealing, cold working, and welding, are inevitable. Therefore, investigation on the material compatibility of the treated material is necessary.

Structural materials are usually subjected to different levels of cold working during final manufacturing stages to increase hardenability. Cold deformation affects the corrosion resistance of stainless steels because planar dislocation arrays [1] and deformation twins are introduced. Other reports related to cold work were mostly done on low cold work degree [2]–[4]. Thus, research on high cold work in liquid metal environment may give comprehensive understanding on its effect, especially, in a liquid metal corrosion. Furthermore, it may be a valuable input for the end user, such as Power Plant Company.
The aim of the present study is to investigate newly proposed ferritic/martensitic type, i.e. YUS409D, of bellows under high-temperature LBE. The static tests were carried out at 500 and 600°C with $2.6 \times 10^{-7}$ and $4.7 \times 10^{-6}$ wt%, respectively, for 500 hours. The bellows of a bellow-sealed valve are high cold work component, which plays an important role as to protect a spring from corrosion, to eliminate the effect of back pressure during pressure relief, etc.

2. Experiment

The YUS409D is the new development ferritic/martensitic bellows to be used in LBE environment. Ni content was not used as alloying element to prevent from preferential dissolution. SS316L is popular material to be used as bellows material. In detail of the chemical composition is shown in Table 1. For fabrication of the bellows, the material is undergoing repeated cold working following by annealing. Bellows is a double layer cold worked material with 80% of total cold work degree. However, the cold work treatment was done step-by-step for reducing the thickness and increasing the hardness, and then annealing was done in between of cold work for the purpose of softening the material. The cold work process was carefully done to maintain the ductility of the bellows. The image of the bellows is shown in Fig. 1. In detail process of making the bellows is not revealed due to some restrictions.

| Material   | Fe   | C   | Cr | Ni  | Mo  | Mn  | Si  | P  | S  | Ti  |
|------------|------|-----|----|-----|-----|-----|-----|----|----|-----|
| YUS409D    | Balance | 0.005 | 11 | -   | -   | 0.34 | 0.44 | 0.024 | 0.002 | 0.19 |

Figure 1. Image of bellows of bellow-sealed valve

The corrosion tests were conducted in stagnant LBE at 500 and 600 °C for 500 hours. The oxygen concentration (OC) was controlled by injection of $4\%H_2+Ar/Ar/Steam$ to achieve $2.6 \times 10^{-7}$ and $4.7 \times 10^{-6}$ of oxygen partial pressure at 500 and 600 °C, respectively. Figure 2 shows oxygen concentration condition on oxygen potential diagram of oxides. It shows that the test conditions were in oxidation zone, i.e. between $Fe_2O_3/FeO$ line and $PbO$ line. The OC was measured by using oxygen sensor. In detail description of the apparatus is shown in ref. [5].
Figure 2. Image of bellows of bellow-sealed valve

After corrosion test, the bellows was rinsed by glycerol at 130ºC and then continued with water cleaning at 80ºC. The bellows were cut in the middle and mounted in the resin. For observation purpose, the cross-section was polished by abrasive paper up to #2400. For grain boundary observation, the cross-section was etched by glycercia etching solution. The planimetric method of ASTM E 112-10 standard test method was used for determination of average grain size. Optical microscope and SEM/EDX were used for the investigation of the corrosion behavior.

3. Results and discussion

3.1. Microstructure profiles

The grain boundary profiles were measured using 3-5 figures from the different location. In accordance to Fe-Cr system phase diagram, the corrosion test temperature, i.e. 500 and 600 ºC, will not change the martensitic phase of the YUS409D (11wt% of Cr).

Figure 3 shows optical micrographs of grain boundary profile of bellows from the post-test specimen. The DIN1.4313, DIN1.4922, and Optifer-IX, that are ferritic/martensitic steel [6], were chosen to be compared with YUS409D result due to comparable chemical content. The DIN1.4313 (FJZ) has 13wt%Cr and 4.0wt%Ni. The DIN1.4922 (FJZ) has 11.5wt%Cr and 0.5wt%Ni, while Optifer-IX has 8.9wt%Cr with no Ni content. It is reported that average grain size for DIN1.4313, DIN1.4922 and Optifer-IX are 76±7, 81±5 and 55±10 µm, respectively. Average grain sizes of the materials are higher than an average grain size of YUS409D, i.e. 39±9 µm. The low percent of cold working induces material by increasing dislocation density. On the other hand, high cold work induces material by recrystallization, which reduces the dislocation density and forms small new grains [7].
Titanium is present as an alloying element for carbide stabilization during a welding process. It is reported that adding titanium will prevent intergranular corrosion by forming carbide in preference to chromium-rich precipitates. Thus chromium-depleted zone formation is prevented [8]. This capability of preventing intergranular corrosion is particularly important for bellows of bellow-sealed valve. During operation, bellows of a bellow-sealed valve will experience low-fatigue cycle, in which an intergranular crack may occur [9]. At this condition, i.e. low-cycle fatigue, intergranular crack formation may be accelerated by intergranular corrosion. Transmission electron microscopy (TEM) is needed for observing the titanium carbide in more detail.

3.2. Oxide layer formation

Fig. 4 shows SEM micrographs of cross section of bellows after corrosion in liquid LBE at 500ºC for 500 h. The SEM image shows a two-layer on the surface. The outer layer had a porous appearance and penetrated with LBE. The inner layer seems to be dense and no LBE penetration. The average oxide layer thickness was about 13 µm. It also shows the EDX result with confirmation of duplex oxide layers. The outer layer is enriched by Fe and O, while the inner layer is enriched by Fe, Cr and O. According to the previous studies, magnetite and Fe-Cr spinel are most likely to form on the martensitic steels [10]–[13]. LBE penetrated through magnetite layer until the interface of magnetite/spinel. However, LBE was prevented to penetrate into spinel layer to have direct contact with the bulk material. The magnetite is porous and prone to LBE penetration, while Fe-Cr spinel is denser compared to magnetite [14]. Fe-Cr spinel layer had some cracks probably due to mechanical treatment after corrosion test.
Figure 4. Cross section of the oxide layers on YUS409D surface after corrosion test at 500°C (SEM and EDX result)

Fig. 5 shows SEM micrographs of cross section of bellows after corrosion in liquid LBE at 600°C for 500 h. The sample clearly shows three layers on the surface. The middle layer seems to be denser than the outer. In comparison with the test at 500°C, most of the oxide layers grew of about twice, i.e. about 32 µm. The EDX measurement shows the existence of Fe and O, i.e. magnetite, in the outer layer. Fe, Cr and O are detected in the middle layer, i.e. Fe-Cr spinel layer. However, the inner layer shows enrichment of Cr and O, and dissolution of Fe. A small portion of LBE is penetrated through magnetite. It is reported that uniform penetration of LBE occurs in LBE corrosion test at temperatures 400-600 C [15].
Figure 5. Cross section of the oxide layers on YUS409D surface after corrosion test at 600°C (SEM and EDX result)

The temperature has a great influence on the oxidation rate of YUS409D bellows. The oxidation thickness increases with increasing exposure temperature. The YUS409D bellows show thicker oxide formation at 600°C than at 500°C. The oxide thickness at 600°C is 2-3 times that at 500°C. Diffusivity of alloying elements, e.g. Cr, Fe, increases at higher temperature, thus accelerates the layer formation.

3.3 Oxidation rate

For determination of the corrosion layer thickness as a function of temperature and time of the experiments, backscattered electron images from SEM and X-ray line from EDX were used. The estimated corrosion rate OR then calculated using the determined layer:

\[ OR = \frac{h}{t} \text{μm/year} \]

H is the layer thickness at temperature T and immersion time t. The corrosion layer was summation of combination of the selective metal oxide, i.e. Fe and Cr, and diffusion zone.

The estimation of corrosion rate in comparison to other ferritic/martensitic steel, i.e. HT9 and T91, and to austenitic stainless steel, i.e. AISI 316L, is shown in Table 2. The results of HT9, T91, and AISI 316L were calculated using correlation in reference [16]. The YUS409D bellows show much higher oxidation rate in comparison with other selected results. Also, a hundred centigrade increased of temperature results in double of oxide layer formation on cold worked YUS409D. It is predictable since YUS409D is highly cold-working materials, while the other results are without cold work. The YUS409D, i.e. bellows of bellow-sealed valve material, is presently proposed to be used in Tokyo Institute of Technology’s LBE loop apparatus [17]. Time operation of the LBE loop apparatus were
about 1000 hours. Thus, utilization of the YUS409D is still applicable for this condition. However, for long time operation, i.e. more than 3600 hours, utilization of the material under oxidation condition should be avoided. The merit of the specimen is on non-utilization of nickel as an alloying element, where previous bellows material was austenitic stainless steel, i.e. nickel base material. Nickel as an alloying element will induce preferential dissolution under LBE environment [15]. Further investigation at reduction or dissolution is needed. Also, investigation on austenitic steel with the same heat treatment is important for comparison.

| Material | Temperature | Oxidation rate (um/year) | Reference |
|----------|-------------|--------------------------|-----------|
| YUS409D  | 500         | 220                      | this study|
|          | 600         | 570                      | this study|
| HT9 and T91 | 500     | 49.7                     | ref.[16] correlation |
|          | 600         | 166.5                    | ref.[16] correlation |
| AISI316L | 500         | 80.4                     | ref.[16] correlation |
|          | 600         | 269.4                    | ref.[16] correlation |

The cold working seems to give effects on oxide layer formation. Previous studies on pure iron show that oxidation rate is increasing due to cold work in several environments, such as O2, water vapor and CO2. Caplan et. al reported that rapid oxidation rate of cold worked pure Fe is due to extra dislocation [2]. Extra dislocation can act as vacancy sink that inhibits the formation of pore belt at the metal/oxide interface. Since, the pore belt can restrain the diffusion of iron, which means a decrease in the oxidation rate. In this study due to high cold work degree, i.e. 80%, most likely phenomena were not only dislocation and small defect but also re-crystallization. Indeed, annealing is included in the process for relieving stress, but due to heavy cold work re-crystallization may form near the surface or in the whole bulk. Grain density per unit area, which was increased due to re-crystallization, leads to increase of oxygen ion transport through grain boundary. Small grain size, i.e. high number of grain boundaries, leads to increasing of oxidation rate due to high diffusion rate [18]. Vicente et. al reported that when the grain size became small due to heavy cold work, i.e. cold work degree more than 42%, high oxygen transport along grain boundaries occurs as well as rapid outward Cr movement along the grain boundaries [7]. Thus, oxidation attack increased on the cold-worked on low alloy ferritic steel 2.25Cr1Mo in air at 550°C.

The condition of the corrosion test of this study is in the static condition. However, in the real situation, the bellows will experience semi-static LBE, low-fatigue cycle, etc. Thus, comprehensive study is needed to ensure the compatibility. The semi-static LBE environment may give similar phenomena to the stagnant condition. However, the low-fatigue condition may affect the corrosion resistance of the steel. Spall-off of the oxide layer may occured due to low-cycle fatigue. This condition will enhance the probability of LME by LBE penetration. Therefore, it is highly recommended to use this type of bellow-sealed valve under a corrosive temperature of LBE (< 450°C).

In addition, longer corrosion test with various temperature profiles is necessary to be conducted for a better understanding of high cold work treatment.

4. Conclusion
Static corrosion test of bellows, i.e. cold-worked steel, YUS409D in LBE were studied at 500 and 600 °C. The grain size of the YUS409D bellows was found smaller than other ferritic/martensitic with similar components due to high cold work treatment. High density of grain boundaries was contributing to rapid inward oxygen and outward Cr along grain boundaries. Enhancement of temperature gave an effect on the formation of oxide layer. Temperature increases from 500 to 600 °C results in acceleration of layer formation by two times. The oxidation rate of YUS409D bellows was found higher than both without cold worked ferritic/martensitic steel and austenitic stainless steel. For short-term operation, the utilization of the cold worked YUS409D in high-temperature LBE was
applicable. For long-term utilization, next experiment should be conducted taking into account observation of corrosion and mechanical properties.

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