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Research Paper

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A Study on the Galvanic Corrosion for Zirconium with Titanium and 316L Stainless Steel

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Abstract : *The coastal area of Republic of Korea is very clean compared to other countries. In this reason, west coastal area of our country is a good place for breeding up a fish such as shrimp. In winter season, the heating system is required for preventing shrimp death caused by freezing in the farm. The heater in the heating system for fishery's farm is operated very severe combating corrosion due to high accumulation by feeding material and high temperature in heated sea water. Almost all manufactured heaters of STS 316L and Ti material are scrapped every year due to heavy corrosion such a general and crevice corrosion. For comparing the general and galvanic corrosion in new heater material, the test material of Zirconium (Zr), Titanium (Ti) and STS 316L are tested by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), current density-time methods and microscopic examination in a 3.5% NaCl solution. The corrosion potential (Ecor) measured by potentiodynamic polarization for Zr, Ti and STS 316L reveals -198, -250 and -450mV, corrosion current density 0.5, 2.5 and 6.5$\mu A/cm^2$ respectively. The film resistance measured by EIS are Zr 63,000, Ti 39,700 and 316L 3,150Ω, and the current of Zr-Ti couple is 0.03μA, whereas Zr-316L SS is 0.1μA. According to the result of this experiment in 3.5% NaCl solution, Zr is excellent corrosion resistance material than Ti and STS 316L.*

Key Words : *Heater, Zirconium, Titanium, STS 316L, Potemtiodynamic polarization, Electrochemical impedance spectroscopy*

1. Introduction

Zirconium alloys have been extensively used as materials for fuel elements in nuclear reactor systems due to their low thermal neutron adsorption cross-section, excellent corrosion resistance and good mechanical property at high temperatures. Titanium is a chemical element with the symbol Ti and atomic number 22. It has low density with a strong, lustrous, corrosion resistant (including sea water, aqua regia and chlorine). Ti is transition metal with a silver color. STS 316L is an austentic chromium-nickel stainless steel containing molybdenum. This addition increases general corrosion resistance, improves resistance to pitting from chloride ion solutions, and provides increased strength at elevated temperatures. Typical uses include exhaust manifolds, furnace parts, heat exchangers, valves, chemical equipments, tanks, evaporators, and parts exposed to marine atmospheres.

The coastal area of Republic of Korea is very clean compared to other countries. In this reason, west coastal area of our country is a good place for breeding up a fish such as shrimp. In winter season, the heating system is required for preventing shrimp death caused by freezing in the farm. The heater in the heating system for fishery's farm is subjected to severe condition combating corrosion due to high feeding material accumulation and increased seawater temperature. Almost all manufactured heaters of STS 316L and Ti material are scrapped every year due to heavy corrosion such a general and crevice corrosion. For comparing the general and galvanic corrosion in new heater material, the test material of Zirconium (Zr), Titanium (Ti) and STS 316L are tested by potentio-dynamic polarization, electrochemical impedance spectroscopy (EIS), current density vs time methods (IT) and microscopic examination in a 3.5% NaCl solution. The results of this paper will promote the design for heater and concerned industries.

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2. Material and experimental procedure

2.1 Materials for experiment

Materials for experiment are Zr, Ti and STS 316L, and were purchased at material market in Korea. Chemical composition for Zr is Hf 0.7, Fe 0.07, H 0.003, N 0.005, C 0.01, O 0.014wt.% and the balance is Zr. For Ti, it is C 0.01, Fe 0.06, H 0.0011, N 0.004, O 0.015 and the balance Ti while STS 316L have C 0.02, Si 0.45, Mn 1.13, P 0.04, S 0.022, Ni 13.47, Cr 16.22, Mo 2.15, Cu 0.28 and balance is Fe.

The specimen dimensions to be used for polarization test are 10mm × 20mm × 2mmt for Zr, Ti and STS 316L. All specimens are mounted by Epoxy except the outside upper surface. Fig. 1 shows the Shape of mounted specimens of Zr, Ti and STS 316L. The surface is polished with #2,000 emery paper, and alumina oxide to acquire mirror like surface.

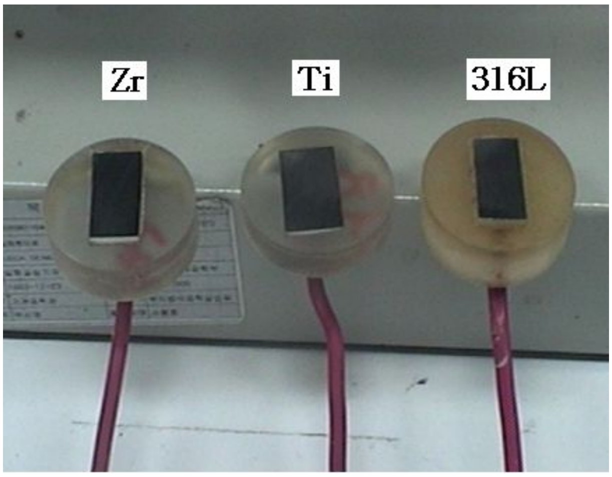

Fig. 1. The shapes of mounted specimens (10 × 20 × 2mmt).

2.2 Facilities of experiment and test methods

For comparing the corrosion resistance in sea water, 3.5wt% NaCl solution was adopted to all experimental solution such as potentiodynamic polarization, EIS and IT test. Potentiostat for measuring potentiodynamic polarization is CMS-100 made in Gamry Co. electrochemical impedance spectroscopy (EIS) made in CMS-300, and IT measuring system is CMS-105 program. For comparing the corrosion tendency of test materials, the potentiodynamic polarizations are scanned from -1,000mV to +1,500mV (vs calomel electrode: SCE) with scan rate 2mV/second. EIS experiment are conducted from 5,000Hz to 0.02Hz under the constant applied potential as natural state for the specimen that are finished potentiodynamic polarization. Current density vs Time (IT) curve are used Zero Resistance Ammeter (ZRA) with the Zr electrode as references. The distance of two pole (namely Zr-Ti and Zr-STS 316L are connected with 50mm gap. The current density is measured to 18,000sec. (5hours) according to time pass. Same technique was adapted by another researcher for corrosion(Baik, 2004; Yoo et al., 2009). Metallurgical microscopes are used to examine the surface of completed experimental specimen.

3. The results and discussion

3.1 Potentiodynamic polarization

Fig. 2 shows potentiodynamic polarization curves for Zr, Ti and STS 316L in 3.5% NaCl solution. In Fig. 2, the Ecor are measured as Zr -198, Ti -250 and STS 316L -450mV respectively. Similar methods are reported with useful meaning for corrosion research by Mondal and Mogoda(Mondal et al., 2005; Mogoda, 1999). The corrosion current densities (Icor) are measured as Zr 0.5, Ti 2.5 and 316 SS 6.5μA/cm^2. The corrosion rate is calculated as mm/year = 3.268(M/dn) × Icor, where M is molecular mass (g), d is density (g/cm^3), n is mole number of transferred electron, and Icor is corrosion current density (mA/cm^2). The calculated value for each materials are Zr 0.006, Ti 0.024 and STS 316L 0.051mm/year. The results of potentiodynamic polarization reveal that Zr is more corrosion resistant than Ti and STS 316L. Moya reported that the cause of high corrosion resistant of Zr is the formation of protective film as ZrO_2(Moya et al., 2000). Fig. 3 shows the surface morphology of Zr after potentiodynamic polarization test in 3.5% NaCl solution. In spite of applied high voltage to +1,500mV, the corrosion phenomena is general dissolution type without pitting. Fig. 4 shows the surface morphology of Ti after potentiodynamic polarization test in 3.5% NaCl solution. The surface of Ti is almost same tendency as Zr. Fig. 5 shows the surface morphology of STS 316L after potentiodynamic polarization test in 3.5% NaCl solution. As shown in Fig. 5, although low voltage applied than Zr and Ti, the surface of STS 316L appeared much passive film damage by corrosion with pitting as large as diameter 0.1mm. The cause of high corrosion damage must be a large current density value of 0.8mA/cm^2 under the applied potential of +900mV.

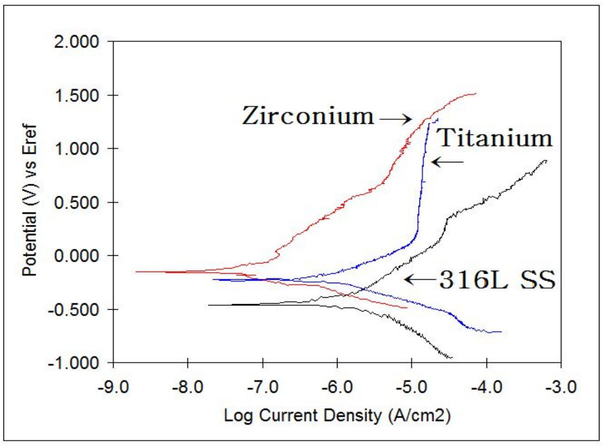

Fig. 2. Potentiodynamic polarization curves for Zr, Ti and STS 316L in 3.5% NaCl solution.

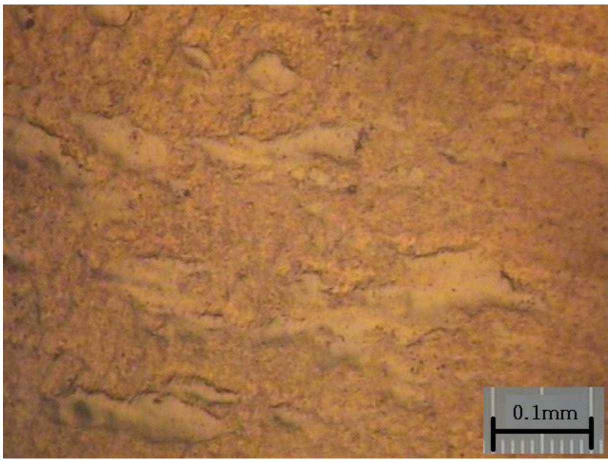

Fig. 3. Surface morphology of Zr after potentiodynamic polarization test in 3.5% NaCl solution.

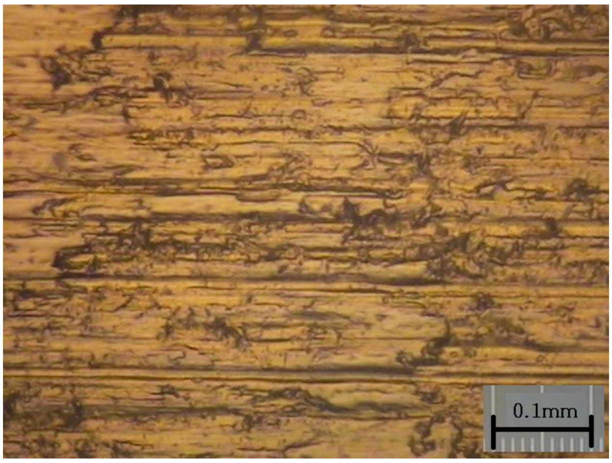

Fig. 4. Surface morphology of Ti after potentiodynamic polarization test in 3.5% NaCl solution.

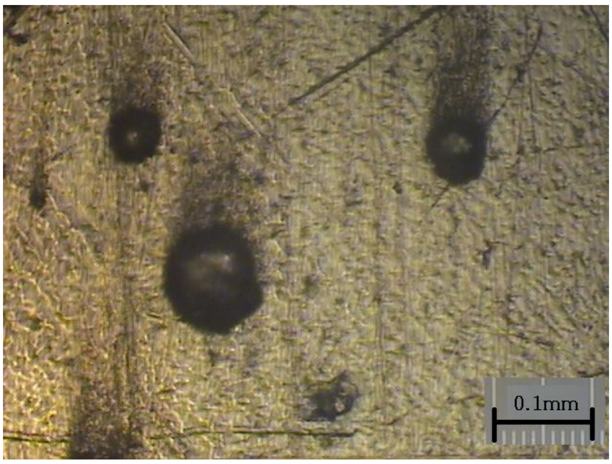

Fig. 5. Surface morphology of 316L after potentiodynamic polarization test in 3.5% NaCl solution.

3.2 Electrochemical Impedance spectroscopy under constant voltage

Fig. 6 shows potentiostatic EIS test result as Bode plot for Zr after polarization test in 3.5% NaCl solution. As shown In Fig. 6, the surface passive film resistance is measured to be 63,000Ω.

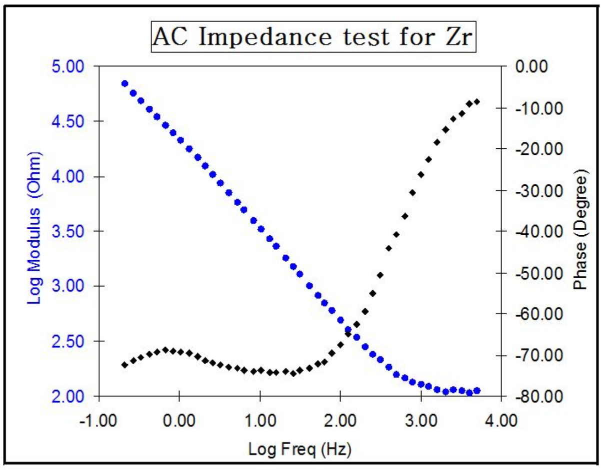

Fig. 6. Potentiostatic EIS Test result for Zr after polarization test in 3.5% NaCl solution.

Fig. 7 shows the Ti test result as same condition as former Fig 6. The surface passive film resistance is measured to be 39,700Ω. Fig. 8 shows for STS 316L that reveals 3,150Ω value. Due to the fact of film resistance is directly connected with corrosion, the higher value indicates the good corrosion resistance. The EIS test results appeared that the Zr have very superior corrosion resistance than that of Ti and STS 316L.

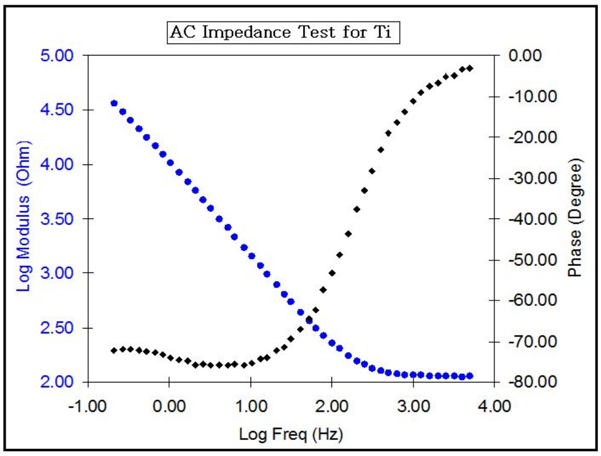

Fig. 7. Potentiostatic EIS test result for Ti after polarization test in 3.5% NaCl solution.

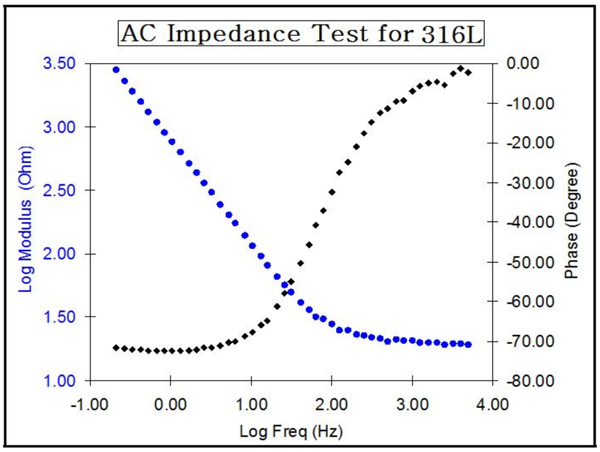

Fig. 8. Potentiostatic EIS Test result for STS 316L after polarization test in 3.5% NaCl solution.

3.3 Current vs Time (IT) experiments

Fig. 9 shows Galvanic current with immersion time for Zr/Ti and Zn/STS 316L pairs in 3.5% NaCl solution. In case of Zr-Ti couple, the initial current is 0.1μA and the value gradually decreases after 5hours immersion to 0.03μA. Another couple of Zr-STS 316L exhibited initial current to be somewhat higher, but the current decreased to 0.1μA in 5hours immersion. Vermoyal and Yingi reported similar methods as corrosion test(Vermoyaletal et al., 1999; Chen et al., 2006). In each couple, the Zr act as cathode and Ti and STS 316L act as anode.

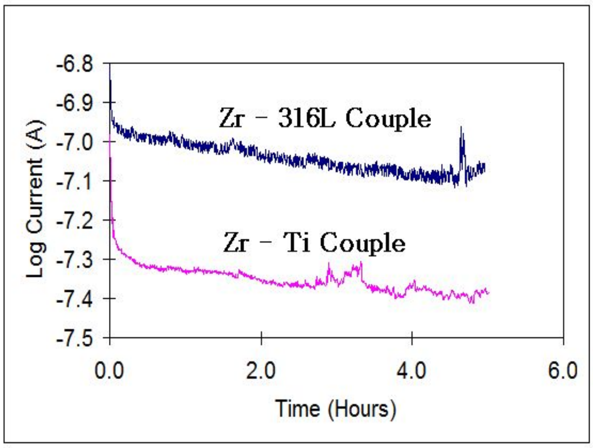

Fig. 9. Galvanic current with immersion time for Zr/Ti and Zn/STS 316L pairs in 3.5% NaCl solution.

The currents flow from Ti and STS 316L to Zr in each case. This means that Ti and STS 316L are corroded, where as Zr is protected from galvanic cell. The current of Zr-STS 316L is higher than Zr-Ti couple due to large difference of voltage, Fig.10 shows the surface morphology of STS 316L after current-time with potentiostatic test in 3.5% NaCl solution. The microstructure of Zr, Ti and STS 316L do not appeared corrosion damage in inspection. This result is somewhat comparable with potentiodynamic polarization that appeared with large pitting in STS 316L as Fig. 5. The reason of such a different result is due to high applied voltage and current density in Fig. 5, where as low voltage difference in Fig. 10.

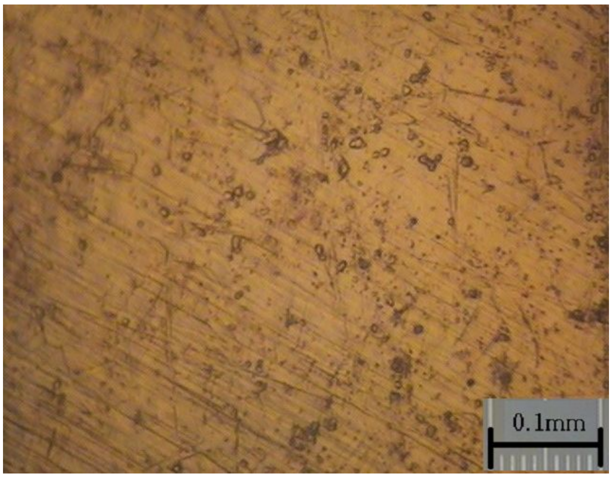

Fig. 10. Surface morphology of 316L after current-time potentiostatic test in 3.5% NaCl solution.

4. Conclusions

For comparing the general and galvanic corrosion in new heater material, the material of Zirconium (Zr), Titanium (Ti) and STS 316L are tested by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), current density vs time methods and microscopic examination in a 3.5% NaCl solution. The result of this experiment confirmed that Zr is excellent corrosion resistance material than Ti and STS 316L. The results of this paper as follows;

1) The Corrosion potentials obtained by potentiodynamic polarization are Zr -198mV Ti -250mV and -450mV, and corrosion current densities are 0.5, 2.5 and 6.5μA/cm^2 respectively. The calculated corrosion rate for each materials are Zr 0.006, Ti 0.024 and STS 316L 0.051mm/year. The corrosion morphologies taken by metallurgical microscopic image reveal that the Zr and Ti are general corrosion type, whereas STS 316L is severe corrosion with

heavy pit. According to the result of this experiment in 3.5% NaCl solution, Zr is excellent corrosion resistance material than Ti and STS 316L.

2) The surfaces film resistances measured by EIS are Zr 63,000 Ω, Ti 39,700Ω and STS 316L 3,150Ω. Due to the fact of the high film resistance resist the electron flow, the Zr is more corrosion resistant than Ti and STS 316L.

3) The measured current obtained by current vs time curve (IT) at 5hours immersion are Zr-Ti couple is 0.03㎂ whereas Zr-STS 316L is 0.1㎂. The Zr acted as cathode in both Ti and STS 316L couple.

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