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Corrosion of titanium in supercritical water oxidation environments ①

LU Jian-shu(卢建树)[1], MAO Zhi-yuan(毛志远)[2], ZHANG Jiu-yuan(张九渊)[1],
MA Chun-an(马淳安)[1], MAO Xin-biao(毛信表)[1], LI Xiao-hua(李肖华)[1]
(1. College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China;
2. College of Materials and Chemical Engineering, Zhejiang University, Hangzhou 310027, China)

[Abstract] Supercritical water oxidation (SCWO) can effectively destroy many kinds of civilian and military wastes. The high temperature and high pressure SCWO operation conditions generate very corrosive environment that many engineering materials fail to withstand. Preliminary test shows that titanium may be a promising material in most of SCWO conditions. Commercially pure titanium is tested in four kinds of SCWO environments. Phenol, sodium dodecyl-benzosulfonate, *n*-amine phenol, and chlorpyrifos were chosen as typical target pollutants. The results show that titanium is only superficially attacked in the first three SCWO environments while in chlorpyrifos SCWO medium titanium is corroded. The corrosion is temperature dependent, with heavier corrosion occurring at near critical temperature. X-ray diffraction analysis shows that the corrosion products consist of titanium oxy- phosphates and titanium oxide, in which $Ti_5O_4(PO_4)_4$ is the main phase.

[Key words] titanium; corrosion; supercritical water oxidation
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1 INTRODUCTION

At present, tremendous amount of organic wastes has been produced in many branches of industry each year. Many of them have hazardous effects to our society. There are many ways to treat these wastes, such as biological treatment and aeration, wet air oxidation, electrochemical oxidation, photo-catalytic oxidation, incineration and landfill. However, none of the methods has sufficient efficiency or no side effects. Supercritical water oxidation (SCWO) is an emerging technology that can completely destroy almost all hazardous wastes in short time[1, 2]. It utilizes the special properties of supercritical water (temperature > 374.2 ℃, pressure > 22.1 MPa): low density, low polarity, low viscosity, and high diffusion rate[3]. Most organic and gases can be dissolved in it and become a single phase. So supercritical water is a perfect medium for oxidizing organic wastes. Actually, for many organic compounds a destruction efficiency of 99.9% can be achieved by SCWO in residence time of 2 min or less.

Unfortunately, corrosion of materials of the equipment of SCWO system has been the main problem that hinders the widespread application of the technology. Corrosion rate of 51 mm per year for 316 stainless steel has been recorded[4]. In the worldwide research of material corrosion resistance in SCWO environments, most of the studies are for stainless steels and nickel base alloys[5]. Only few work has been done for titanium.

In this paper, commercially pure titanium was tested in different kinds of SCWO environments. Phenol, sodium dodecyl-benzosulfonate, n-amine phenol, and chlorpyrifos were chosen as typical target pollutants. Phenol (C_6H_5OH) is a common pollutant. Its molecule has only carbon, hydrogen and oxygen. Organic acid such as formic acid and acetic acid are the intermediate oxidation products[6]. Sodium dodecyl-benzosulfonate ($C_{12}H_{25}$-$C_6H_4SO_3Na$) is an old detergent that contains sulfur in its molecule. Sulfuric acid is one of the intermediate oxidation products. N-amine phenol (H_2N-C_6H_4OH) contains nitrogen in its molecule, so nitric acid is inevitable in the SCWO environment. Chlorpyrifos ($C_9H_{11}OSPNCl_3$) is a pesticide that contains S, P, N and Cl in its molecule. Various kinds of inorganic acids may be produced when it undergoes the oxidation. By testing the corrosion resistance of Ti in each SCWO environment the performance of the metal can be evaluated in more systematic ways.

2 EXPERIMENTAL

2.1 Test facility

To study corrosion of materials in SCWO conditions, a continuous SCWO system which can be operated for long time at supercritical conditions (usually at 25 MPa and at lower than 450 ℃) has been built in our laboratory[7]. Using this system we have carried out many corrosion experiments on stainless steels and nickel

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base alloy[8~10].

2.2 Ti samples and target pollutants preparation

The commercially pure titanium plate of 1 mm thickness was purchased from Baoji Nonferrous Metal Factory. The nominal purity is 99.9%. Samples in size of 10 mm × 20 mm were cut from the plate. All samples were polished with 14 μm SiC paper and were ultrasonically cleaned in 2-propanol. Waste water with 10 g/L target pollutant was prepared before each test.

2.3 Experimental procedure

Two parallel Ti samples were fixed in the reactor of the SCWO system in each test. Samples were weighed before and after exposure. Pure water was first injected into the system by high pressure metering pump. Prepared waste water and high pressure air were then injected into the system when a desired temperature was reached. The exposure duration lasted for a few hours to 188 h according to the corrosiveness of the media.

After the exposure, the samples were first cleaned in running water and then ultrasonically cleaned in 2-propanol. Corrosion rates of the materials were determined by gravimetric method. Corrosion morphology and localized corrosion were examined by optical microscopy and SEM. Corrosion products were analyzed by XPS and XRD.

3 RESULTS AND DISCUSSION

3.1 Corrosion in different SCWO environments

Table 1 shows the general corrosion rates of Ti in different SCWO environments. All the samples show mass gain after exposure. It is obvious that Ti has different corrosion resistance in the four SCWO environments. Ti samples were only superficially attacked in SCWO environments that destroy phenol, sodium dodecyl-benzosulfonate, and n-amine phenol. The surfaces remain smooth after the tests. The corrosion rates are less than 0.1 mm per year. So Ti has sufficient corrosion resistance in these SCWO environments. This means that Ti can withstand both the organic acids and sulfuric acid or nitric acid attacks in SCWO conditions. The reason may be due to the high oxidation nature (sufficient O_2 present to passivate Ti) of the environments. Fig. 1 shows the XPS diagram of a Ti sample exposed in n-amine phenol SCWO environment. The strong O and C peaks show that the surface is covered with dense O and

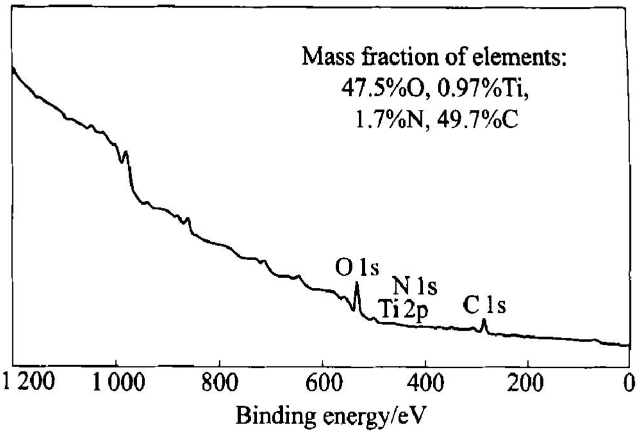

Fig. 1 XPS diagram of Ti sample exposed in *n*-amine phenol SCWO environment

C layer. Small amount of N is also present.

However, Ti samples exposed in chlorpyrifos SCWO environment were apparently corroded. A thin blackish gray layer was formed after the exposure. Corrosion rate based on mass gain was 3.5 mm per year in short test period, more than ten times higher than that in other SCWO environments. This corrosion rate agrees with the data reported by Friedrich[11]. Corrosion product on the Ti sample was analyzed by XRD. Fig. 2 shows the diagram by a step scan XRD technique. Those peaks with '△' sign is for Ti, those peaks with '☆' sign is for $Ti_5O_4(PO_4)_4$, those peaks with '#' sign is for $Na(Ti)_2(PO_4)_3$, and those peaks with '$' sign is for TiO_2. From the diagram, the corrosion product consists of $Ti_5O_4(PO_4)_4$, $Na(Ti)_2(PO_4)_3$ and TiO_2. The main phase is $Ti_5O_4(PO_4)_4$. This is the discovery that is not mentioned before by others.

Table 1 Corrosion of Ti in four SCWO environments

Organic waste (10g/L)	Test time/ h	Temperature/ ℃	Corrosion rate* / ($mg \cdot cm^{-2} \cdot h^{-1}$)	Surface morphology
phenol	188	~ 400	0	Thin gray film
SDB#	48	~ 400	+ 0.007	Thin blackish gray film
N-amine phenol	30	~ 400	+ 0.019	Thin gray film with yellow spots
Chlorpyrifos	4	~ 400	+ 0.178	Microscopically uneven thin layer

*: '+' means sample gaining mass; #: SDB= sodium dodecyl-benzosulfonate

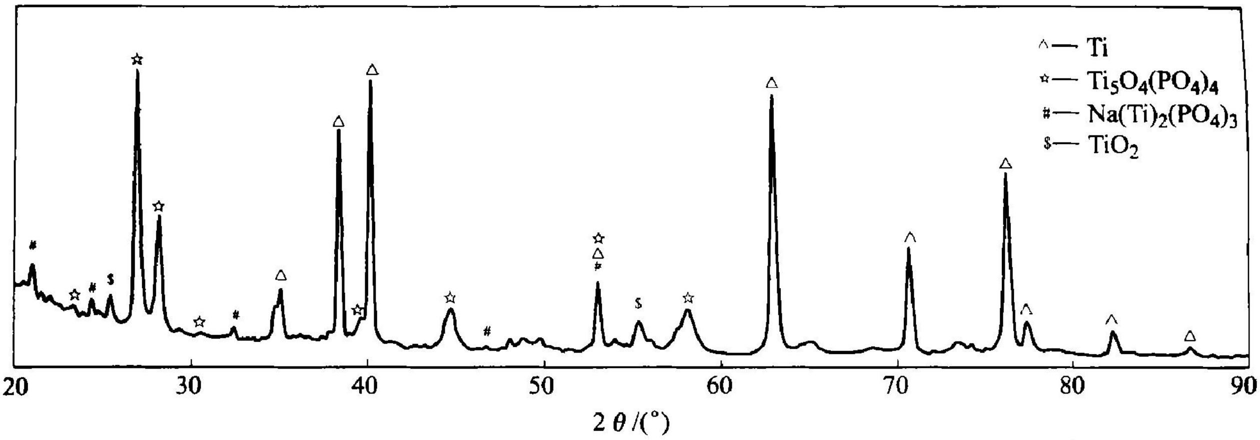

Fig. 2 XRD diagram of Ti corrosion products exposed in chlorpyrifos SCWO environment

Table 2 Corrosion rates of Ti at different temperatures

Temperature/ ℃	150	200	250	300	350	400	450
Corrosion rate/ ($mg \cdot cm^{-2} \cdot h^{-1}$)	+ 0.003	+ 0.01	+ 0.03	+ 0.089	+ 0.159	+ 0.178	+ 0.09
Sample appearance	Gray	Gray	Dark gray	Dark gray	Greenish black	Greenish black	Black

Ti corrosion by halogenide (especially fluoride) is well known[12]. But the Ti corrosion by high temperature phosphorous compound is little reported. The reason for the formation of phosphate corrosion product of Ti in the chlorpyrifos SCWO environment may be due to the insolubility of the phosphate salts in water. The deposition of phosphate layer on Ti surface may form the occulted area between the deposits and the Ti substrate. This area will be corroded locally due to the lack of oxygen and the electrochemical occult cell effect. This postulation is confirmed by the observation of corrosion pits beneath the corrosion product layer (see Fig. 3). The pits are filled with corrosion products, which means that the mass transport of the corrosion process is difficult. This is easy to understand because the corrosion took place under the deposits and surface corrosion products.

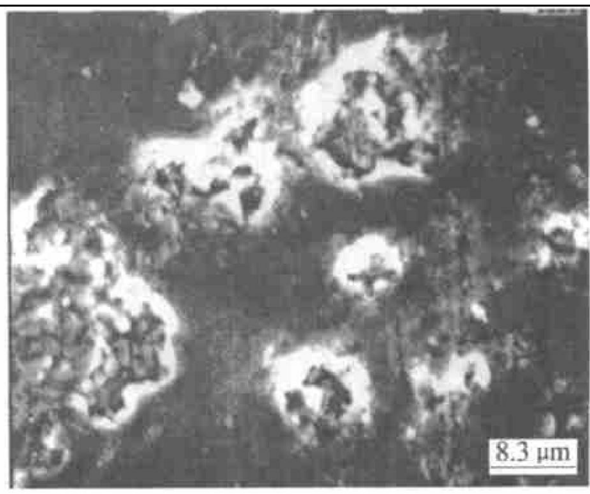

Fig. 3 Pitting corrosion of Ti samples exposed in chlorpyrifos SCWO environment

3.2 Temperature dependence of Ti corrosion in chlorpyrifos SCWO environment

Table 2 shows the results of titanium corrosion at different temperatures. Corrosion begins to take place at temperature higher than 250 ℃. Higher corrosion rates occur around critical temperature (350~ 400 ℃). The Ti samples at 350 ℃ and 400 ℃ show greenish black corrosion products while at 450 ℃ the sample is black. The different colors of the samples suggest different corrosion mechanisms at different temperatures.

SEM examination shows that the corroded samples are microscopically uneven (see Fig. 4). At 300 ℃ the sample shows metallic Ti surface, at 350 ℃ the surface is covered with dense corrosion product, at 400 ℃ the surface covered with porosity is corrosion product, at 450 ℃ the surface is only partially covered with corrosion product. From these photos, it is clear that Ti will suffer most serious corrosion at near critical temperature in the SCWO environment. This is because at far above critical temperature (e.g. 450 ℃) the supercritical fluid becomes a non-polar medium and so reduces its corrosiveness. Another reason is that at lower temperature (< 300 ℃) the organic decomposes little so the concentrations of the corrosive species (e.g. HCl, H_3PO_4, HNO_3, H_2SO_4) are low, while at higher temperatures (> 400 ℃) the organic decomposition is very fast and complete so the residence time of the corrosive species is short.

Fig. 4 SEM photos of corrosion product on Ti surface at different temperatures
(a) —300 ℃; (b) —350 ℃; (c) —400 ℃; (d) —450 ℃

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