EFFECT OF Co CONTENT ON THE CORROSION OF HIGH PERFORMANCE STAINLESS STEELS IN SIMULATED BIO-SOLUTIONS

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Abstract: This work focused on the effect of Co content on the corrosion resistance of high pitting resistance equivalent (PRE), super ferritic, Ni-free stainless steels in simulated bio-solutions. The effect of Co in Ni-free alloys was evaluated by cytotoxicity test. Anodic polarization test and AC impedance measurement were performed to evaluate the effect of Co on corrosion resistance of the alloys. The cytotoxicity test result for 4 experimental alloys shows non-cytotoxic but mild cytotoxic for 316L stainless steel due to relatively poor corrosion resistance. However, the effect of Co on the passivity was positive in bio-solution but it was negative in acidic chloride solution.

Introduction

The biocompatibility of the metallic implant is of considerable concern because such an implant can corrode in an in vivo environment [1, 2]. The consequences of corrosion are the disintegration of the implant material per se, which will weaken the implant, and the harmful effect of corrosion products on the surrounding tissues and organs [1]. Stainless steels have been used widely as the represented bio-metal. Recently, high performance stainless steels with high corrosion resistance to highly acidic chloride environments had been developed. These steels are also called as super stainless steels which contain high Cr, Mo, W, and nitrogen. Pitting Resistance Equivalent (PRE) values indicate the degree of corrosion resistance of stainless steels in chloride solutions, including simulated bio-solutions. In vitro studies have indicated that particulate Co is toxic to human osteoblast-like cell lines and inhibits synthesis of type-I collagen, osteocalcin, and alkaline phosphatase in the culture medium. However, particulate Cr and CoCr alloys are well tolerated by cell lines with no significant toxicity [1, 3].

This work focused on the effect of Co content on the corrosion resistance of high PRE, super ferritic, Ni-free stainless steels in simulated bio-solutions. The effect of Co in Ni-free alloys on the biocompatibility was evaluated by cytotoxicity test. Anodic polarization test, AC impedance measurement, and XPS analysis were performed to evaluate the effect of Co on
Experimental Methods

Alloys were melted in a high frequency, vacuum induction furnace. After vacuum casting, the round sections of the alloys were hot rolled to 3.5 mm, cold rolled to 1.5 mm, annealed at 1050°C and then water quenched. The experimental alloys examined were Fe-22.5Cr-3.5Mo-4.5W-0.17Co (SFCo1) / 4.16Co (SFCo2) / 8.15Co (SFCo3) / 12.1Co (SFCo4). The PRE range was controlled as 40.5~41.6. The experimental alloys were subjected to the anodic polarization and repassivation tests in 50°C, 0.5N HCl + 1N NaCl and 37°C, Hanks’ balanced salt solution by using a Potentiostat (Gamry DC105). The critical pitting temperature (CPT) was measured by a method of ASTM G48-00 [4]. AC impedance was measured for the stainless steels that formed passive film. Four specimens were prepared for each material to perform the cytotoxicity testing and detail method was described elsewhere [5].

Results & Discussion

Since metallic implants can corrode in an in vivo environment, the biocompatibility of the metallic implant is of considerable concern [1, 2] and the cytotoxicity test must be performed before application as bio-materials. The cytotoxicity test result for 4 experimental alloys of the present study showed non-cytotoxicity but mild cytotoxicity for 316L stainless steel due to relatively poor corrosion resistance. In particular the experimental alloys don’t have nickel and were controlled to high PRE of 42 with Co content ranging from 0 to 12%. Anodic polarization test was conducted to evaluate the effect of Co content on the corrosion resistance of the alloys. Figure 1 shows the effect of Co-contents on the anodic polarization behavior of the experimental alloys in deaerated 37°C Hanks’ balanced solution. With increasing Co content, the corrosion potential increased a little while the passive current density decreased. However, the commercial alloy 316L stainless steel showed a level of pitting corrosion under +300mV(SCE). This excellent corrosion resistance that was basically due to the high PRE [6~8] and Co-content which also played a role in the strengthening of the passive film. The positive role on passive film exerted by the Co-content was confirmed in the results of repassivation test and AC impedance measurement. The repassivation indices of the alloys were 0.4441, 0.5046, 0.4834, and 0.5227, respectively, and increasing Co-content increased the repassivation rate in Hanks’ balanced solution. Figure 2 shows the effect of Co contents on the AC impedance of the experimental alloys (passivated 1hr at +100mV(SCE) in deaerated 37°C Hanks’ balanced solution). This result further confirmed the same role of Co-content on corrosion resistance. CPT of 4 alloys in Hanks’ balanced solution was over boiling point regardless of Co contents.

On the other hand, a different tendency of Co-effect was obtained in acidic chloride solutions. Figure 3 shows the effect of Co contents on anodic polarization behavior of the experimental alloys in deaerated 50°C 0.5N HCl + 1N NaCl solution. With increasing Co content, the corrosion potential increased slightly and the passive current density increased, while pitting
corrosion occurred in high Co bearing alloys SFCo3 and SFCo4. In addition, the commercial alloy 316L stainless steel didn’t establish any passivity. Repassivation indices of the alloys were 0.6216, 0.5926, 0.5586, and 0.5541, respectively and increasing Co-content decreased the repassivation rate in acidic chloride solution. Figure 4 shows the effect of Co contents on the AC impedance of the experimental alloys (passivated 1hr at +100mV(SCE) in deaerated 50°C 0.5N HCl + 1N NaCl solution). This result also showed the same role of Co-content on corrosion resistance. CPT of 4 alloys in 6% FeCl3 + 1% HCl solution were 75, 70, 70, and 65°C respectively and increased Co-content reduced the corrosion resistance in acidic chloride solution. Figure 4 shows the effect of Co contents on the AC impedance of the experimental alloys (passivated 1hr at +100mV(SCE) in 50°C 0.5N HCl + 1N NaCl solution). Cobalt in the alloys reduced the AC impedance in acidic chloride solution.

Why does the effect of cobalt in the alloys differ depending upon the corrosion environment?
This behavior seems to be related to the composition of passive film on the surface. The surface of the passive films was analyzed by XPS. The XPS results showed that the ratio of [metal oxide]/[metal + metal oxide] in the film formed in 0.5N HCl + 1N NaCl decreased from 0.54 to 0.35 Co content was increased, while the ratio in the film formed in Hanks’ balanced solution increased from 0.46 to 0.48 due to the increased Co-content. Therefore, since cobalt strengthens the passive film in bio-solution, corrosion resistance improved, whereas that in acidic chloride solution was reduced because of the film-weakening effect of cobalt.

Conclusions
1. The cytotoxicity test result for 4 experimental alloys showed non-cytotoxic but mild cytotoxic for 316L stainless steel due to relatively poor corrosion resistance. This behavior is related to the high corrosion resistance of Ni-free experimental alloys having PRE of 42, regardless of Co-content.
2. Increasing Co-content in Ni-free stainless steels, passive current density reduced, and repassivation rate and AC impedance increased in bio-solution. However, the increased Co-content increased the passive current density, but decreased the repassivation rate and AC impedance in the acidic chloride solution.
3. With increasing Co content in the alloys, the ratio of [metal oxide]/[metal + metal oxide] increased in the bio-solution but decreased in the acidic chloride solution. Therefore, the corrosion resistance was improved in the bio-solution because cobalt strengthens the passive film, but it deteriorated in the acidic chloride solution because cobalt weakens the film.

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