Microstructure and anodic polarization behavior of experimental Ag–18Cu–15Pd–12Au alloy in aqueous sulfide solution

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The anodic corrosion behavior of an experimental Ag–15Pd–18Cu–12Au alloy in 0.1% Na₂S solution in relation to its microstructure was investigated using potentiodynamic and potentiostatic polarization techniques with analyses of corrosion products by X-ray diffractometry, Auger electron spectroscopy, and X-ray photoelectron spectroscopy. The role of Pd in improvement of the corrosion resistance was also investigated.

In the potential/current density curve, three distinct current peaks, at −520 mV (peak I), −425 mV (peak II) and −175 mV (peak III), were observed. The Ag-rich $\gamma_1$ matrix with coarse Cu and Pd-rich lamellae was the most corrosion-susceptible region, and this region was preferentially corroded at peak I with the formation of granular deposits of Ag₂S. A small amount of Ag–Cu mixed sulfide deposited on the Cu and Pd-rich coarse particles and dissolution of Ag as AgO⁻ might have occurred in parallel with Ag₂S formation at peak II. Enrichment of Pd on the alloy surface occurred at peak III due to preferential dissolution of Ag and Cu. A high level of corrosion resistance was attained with the formation of a thin Pd-rich sulfide film, which enhanced the passivity of the alloy in an alkaline sulfide solution. It was found that passivity is an important phenomenon not only for base metal alloys but also for noble metal alloys to maintain high levels of resistance to corrosion and tarnishing in sulfide environments.

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1. Introduction
Ag–20Pd–(10-20)Cu–12Au alloys have been widely used in Japan as alternatives to expensive Au casting alloys for cast inlays, crowns and bridges because the cost of dental treatment using an Ag-based alloy, but not that using an Au-based alloy, is covered by the national health insurance. The properties of Ag-based alloys generally satisfy the requirements of a dental casting alloy, but these alloys are more susceptible than are Au-based alloys to corrosion and tarnishing, especially in the presence of sulfide and hydrogen sulfide ions [1, 2].

The corrosion behavior the Ag-based alloys in sulfide solutions has mainly been investigated from the viewpoints of assessment of susceptibility to tarnishing by means of microscopical observations of the attacked component phases or measurement of the color vector change due to the formation of insoluble corrosion products [3-7]. Niemi and Holland [3] examined the attacked structural components of an Ag–24.5Pd–13.5Cu–5.3Au alloy after exposure to an aqueous 2% Na₂S solution using SEM and light optical microscopy, and they found that Cu- and Pd-rich components had greater resistance to corrosion than did the Ag-rich component. German et al. [5] evaluated the resistance to tarnishing of 11 commercial noble metal alloys, including Ag-based alloys, with different noble metal contents and demonstrated that below approximately 55 at% noble metal (Au, Pt, and Pd) content, microstructure plays a dominant role in determination of resistance to tarnishing.

Although the electrochemical potentiodynamic polarization technique can provide useful information on corrosion behavior over a wide range of potentials, there have been few studies in which this technique was used to investigate the corrosion of Ag-based alloys in sulfide solutions. In a previous study, we obtained the potentiodynamic polarization curves for commercial Ag-Pd-Cu-Au alloys with different compositions in 0.1% Na₂S solution and demonstrated that the anodic current density peaks observed between −500 and −375 mV (vs. Ag/AgCl) became smaller with an increase in Au content [8]. Iijima et al. [9] also reported
that the anodic current density for an Ag–20.1Pd–16.5Cu–12.1Au alloy in 0.1% Na₂S solution in the potential range of 0 to +500 mV (vs. Ag/AgCl) was markedly larger than that for an Ag–20.8Pd–17.9Cu–18.3Au alloy, and they concluded that the addition of Au improved the resistance to corrosion and tarnishing in a sulfide environment. Holland demonstrated that the potentiotdynamic polarization curve for an Au–31Ag–9.4Cu–4.1Pd–1.0In alloy in 2% Na₂S solution was markedly different from that in artificial saliva [10]. Several characteristic current density peaks were observed in those anodic polarization curves, but the assignment of reactions that occurred at potentials at which these current density peaks were observed has not been completely accomplished.

The present study was designed to obtain a more thorough understanding of the anodic polarization behavior of dental Ag–Cu–Pd–Au alloys in 0.1% Na₂S solution in relation to their microstructure. We employed an experimental Ag–18Cu–15Pd–12Au alloy, and the reactions involved at different potentials were investigated on the basis of the thermodynamic data and by analyses of corrosion products using X-ray diffractometry (XRD), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) after potentiotstatic polarizations. The role of Pd in improvement of the corrosion resistance was also investigated.

2. Experimental method

2.1. Materials

A Ag–18Cu–15Pd–12Au (mass %) alloy ingot was made from metals with purities of more than 99.9% in a high-frequency induction furnace under an Ar gas atmosphere. The alloy was cast in a 12 × 12 × 1 mm³ plate by a vacuum/pressure casting machine. After casting, the alloy specimens in a gypsum-based mold were bench-cooled to room temperature. The surface of the specimen was metallographically polished with SiC papers and then by 3 μm Al₂O₃ paste. The polished specimens were cleaned ultrasonically in deionized water for 1 min and then dried with oil-free compressed air.

2.2. Metallurgical examination

The polished alloy was etched in an aqueous solution containing 5% KCN and 5% (NH₄)₂S₂O₈, washed with deionized water, and then dried with compressed air. The microstructure of the alloy was examined using an electron probe microanalyzer. The crystal structure of the alloy was examined using an X-ray diffractometer with Ni-filtered Cu Kα-radiation generated by 35 kV accelerating voltage and 20 mA anode current. The diffraction pattern was obtained with a scanning speed of 1°(2θ)·min⁻¹.

2.3. Electrochemical corrosion tests

2.3.1. Potentiotodynamic polarization measurement

Anodic potentiotdynamic polarizations of the Ag–18Cu–15Pd–12Au alloy were carried out in deaerated 0.1% Na₂S solution ([Na₂S] = 1.3 × 10⁻⁴ M, pH = 12). A Ag/AgCl electrode (saturated KCl) was used as the reference electrode and a Pt wire was used as the counter electrode. A fresh solution was made for each measurement and was deaerated by bubbling ultrapure Ar gas for at least 60 min before sample introduction in the cell and throughout the period of the potentiotdynamic polarization measurement. The potentiotdynamic polarization was started from the free corrosion potential at a scan rate of 0.17 mV·S⁻¹. Anodic potentiotdynamic polarizations of pure Au and a commercial alloy (Ag 49%, Pd 20%, Cu 18%, Au 12%, others 1%) were also carried out for comparison. The electrochemical cell temperature was always kept at 37 ± 0.5°C.

2.3.2. Potentiotstatic polarization testing

The electrode potential of the alloy specimen was maintained in deaerated 0.1% Na₂S solution at specific potentials at which distinct current peaks were observed in a potential/current density curve. The surface of the alloy specimen after the potentiotstatic polarization was observed by a scanning electron microscope to examine the corrosion morphology. The corrosion products that had formed on the alloy specimen were analyzed by XRD. An X-ray diffractometer (2013, Rigaku Co. Ltd., Tokyo, Japan) with Ni-filtered Cu Kα-radiation (35 kV, 20 mA) was used. The patterns were recorded with a scanning speed of 1°(2θ)·min⁻¹. Small corrosion products of approximately 0.5 μm in diameter were analyzed using an Auger electron spectrometer (Model 650, Perkin Elmer, Norwalk, USA). Auger spectra were obtained at 20 kV electron beam voltage and 4.4 nA electron current with a beam diameter of 20 nm. The low electron beam current was intended to minimize sample damage. The surface of the alloy after potentiotstatic polarization was also examined by XPS. XPS spectra were obtained using an XPS (ESCA-850, Shimadzu Co. Ltd., Kyoto, Japan) with Al Kα-radiation operated at 7 kV accelerating voltage and 30 mA current under a vacuum of 1 × 10⁻⁶ Pa. The binding energy scale was calibrated by the Au 4f7/2 and Cu 2p3/2 peaks at 83.8 and 932.8 eV, respectively.

3. Results

3.1. Microstructure

Fig. 1 shows a secondary electron image of the etched Ag–18Cu–15Pd–12Au alloy in an as-cast condition and characteristic X-ray images of Ag L₂, Cu L₂, and Pd L₂. The alloy consisted of four different microconstituents: coarse particles with irregular shapes (a), Widmanstätten precipitates (b), fine and coarse precipitate lamellae (c), and matrix. Microprobe analyses showed that the coarse particles were rich in Cu and Pd and depleted in Ag. A characteristic X-ray image of Au Kα showed that there had been no segregation and that the Au was evenly distributed throughout the alloy structure. Fig. 2 shows the X-ray diffraction pattern of the Ag–18Cu–15Pd–12Au alloy in an as-cast condition. The diffraction peaks for the three phases, Cu-rich fcc (12), Ag-rich fcc (22) and bcc PdCu (3) ordered phases, can be seen in the figure.