Effect of microstructure on the corrosion behaviour of dental gold alloys

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The effect of microstructure on the corrosion behaviour of Au–Cu–11 at% Pd, Au–Cu–11 at% Ag and (Au–Cu–11 at% Ag)–5 at% Pd alloys was studied by anodic potentiodynamic and potentiostatic polarization tests. The single-phase Au–Cu–11 at% Pd alloys had high corrosion resistance and their potentiodynamic polarization curves were simple. The high-nobility Au–Cu–11 at% Ag alloy displayed high corrosion resistance regardless of its microstructure. The two-phase Au–Cu–11 at% Ag and (Au–Cu–11 at% Ag)–5 at% Pd alloys had lowered corrosion resistance compared with the single-phase alloys. Anodic potentiodynamic polarization curves of the two-phase alloys were complex, but they were explained by superimposing the curves of each phase using the principle of additivity. The potential at which the current density sharply increased corresponded with that of each phase, and the value of current density was calculated as the sum of the current density of each phase and taking account of their volume fractions. In the anodic potentiodynamic polarization, there was little galvanic effect between the two phases.

1. Introduction

Chemical stability, especially corrosion resistance, is an important property for dental alloys. Corrosion resistance is commonly evaluated by various electrochemical corrosion tests. Many investigations on the corrosion resistance of commercial dental alloys are performed, but it is not easy to understand their corrosion characteristics because of the complex components and phase structure. The chemical composition and microstructure of the alloy will have a great influence on the corrosion behaviour. German *et al.* [1] suggested that corrosion of the Au–Ag–Cu ternary alloys could be enhanced by the formation of a second phase. Corso *et al.* [2] showed that nobility (the total amount of precious elements) determined the overall corrosion resistance for gold-base alloys, but alloying with copper induced silver segregation, resulting in a higher corrosion rate. Many investigators have also reported that the existence of a silver-containing phase or compound resulted in lowered corrosion resistance [3–8].

Potentiodynamic polarization is useful for understanding the corrosion behaviour of alloys over a wide range of potentials, but it only provides qualitative information on the corrosion characteristics. The potentiodynamic polarization curve of a two- or multiphase alloy is complicated, so that it is usually difficult to explain the corrosion behaviour of these alloys. Moreover, the corrosion of a two-phase alloy can be enhanced by the galvanic effect between anodic and cathodic phases. In the case of a forced anodic potentiodynamic polarization test, however, it can be considered that there is little galvanic effect taking place between the two phases. Therefore, the corrosion behaviour of a two-phase alloy is characterized by that of each phase. The potentiodynamic polarization curve of the two-phase alloy should be closely related to that of each phase.

In this study, potentiodynamic curves were generated for Au–Cu–11 at % Pd, Au–Cu–11 at % Ag and (Au–Cu–11 at % Ag)–5 at % Pd alloys and these were used to explain the complex polarization curve of two-phase alloys by superimposing simple curves of each phase. Anodic potentiostatic polarization was also carried out to evaluate the corrosion resistance of these alloys.

2. Experimental procedure

Seven experimental alloys were used in this study (Table I). These alloys were made from 99.99% Au, Ag, Cu and Pd in evacuated quartz ampullae using a high-frequency induction furnace. They were cast into billets of 5 mm × 5 mm × 2 mm by the dental casting technique in an argon atmosphere. A single-phase structure (α_0) and an $L1_0$ type ordered structure of the alloys II, I and III were obtained by solution treatment at 800 °C and heat treatment at 300 °C, respectively [9]. A single-phase structure (α_0) and a two-phase structure, consisting of a Cu-rich α_1 phase and an Ag-rich α_2 phase of the alloys II-Ag, I-Ag, III-Ag and III-Ag + 5Pd were obtained by solution treatment at 800 °C and heat treatment at 300 °C, respectively [10]. Fig. 1 shows a scanning electron micrograph of the two-phase structure consisting of fine lamellae of α_1 and α_2 phases. These specimens

TABLE I Chemical compositions of the alloys used

Specimen	Composition (at %)				Composition (wt %)			
	Au	Cu	Ag	Pd	Au	Cu	Ag	Pd
II	46.0	43.0		11.0	69.9	21.1		9.0
I	37.0	52.0		11.0	61.0	28.1		9.9
III	26.0	63.0		11.0	49.7	38.9		11.4
II-Ag	46.0	43.0	11.0		69.8	21.1	9.1	
I-Ag	37.0	52.0	11.0		61.9	28.0	10.1	
III-Ag	26.0	63.0	11.0		49.7	38.8	11.5	
III-Ag + 5Pd	24.7	59.8	10.5	5.0	47.1	36.8	11.0	5.1
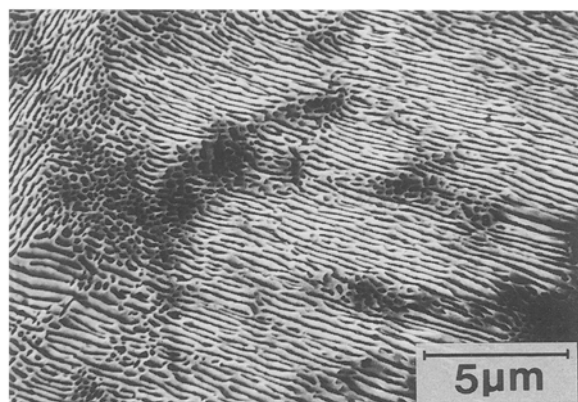
Figure 1 Scanning electron micrograph of III-Ag aged at 300 °C.

Figure 2 Anodic potentiodynamic polarization curves of alloy III in (——) homogenized and (– – –) heat-treated states.

Figure 3 Anodic potentiodynamic polarization curves of alloys (——) II-Ag, (— —) I-Ag, (— · —) III-Ag and (– – –) III-Ag + 5 Pd in the homogenized state.

were embedded in epoxy resin and polished by the metallographic technique. Deaerated 1% NaCl solution at 37 °C was used for corrosion tests. A platinum counter electrode and an Ag/AgCl (KCl saturated) reference electrode were used (E(SCE) = E(Ag/AgCl) − 48.4 mV). Potentiodynamic polarization tests were carried out between − 300 V and + 1000 mV at a scanning rate of 1 mV s^{-1}. Potentiostatic polarization tests were performed for 600 s at 700 mV, at which the electrochemical reactions of constituents except for gold could be accelerated. The integrated current density (denoted by Q) obtained by a potentiostatic polarization test corresponds to the total amount of electrochemical reactions proceeding in the specimen surface. The corrosion resistance can be evaluated from the value of Q [11].

3. Results

3.1. Anodic potentiodynamic polarization curves

Fig. 2 shows the anodic potentiodynamic polarization curves of alloy III in the homogenized and heat-treated states. This alloy has a single-phase structure of α_0 solid solution in the homogenized and a L1$_0$ type ordered structure in the heat-treated states. Their polarization curves were almost the same and the potential (E_c) at which the current density sharply increases (indicated by an arrow in Fig. 2) came out at higher than 700 mV. Small peaks of current density at around 300 mV seemed to be associated with the dissolution of copper existing in the alloy surfaces. The
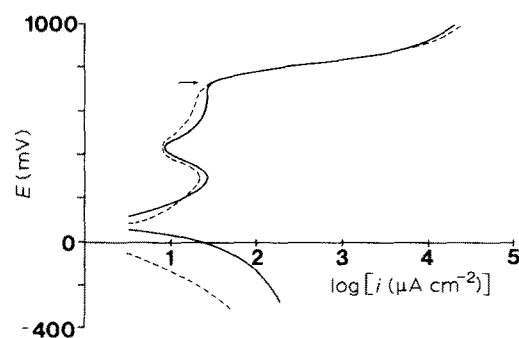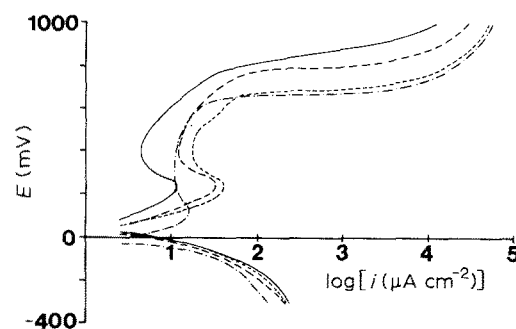
polarization curves of alloys II and I were similar to those of alloy III.

Figs 3 and 4 show the anodic potentiodynamic polarization curves of the alloys II-Ag, I-Ag, III-Ag and III-Ag + 5Pd in the homogenized and heat-treated states, respectively. These alloys have a single-phase structure of α_0 solid solution in the homogenized state and a two-phase structure of α_1 (Cu-rich) and α_2 (Ag-rich) in the heat-treated state. The anodic potentiodynamic polarization curves of the alloys with single-phase structure were simple (Fig. 3), and E_c shifted to a positive potential as the alloy nobility increased. Those of the alloys with two-phase structure were complex (Fig. 4), and E_c appeared at two different potentials. Small peaks of current density at around 200 mV seemed to be the same as those of alloy III.
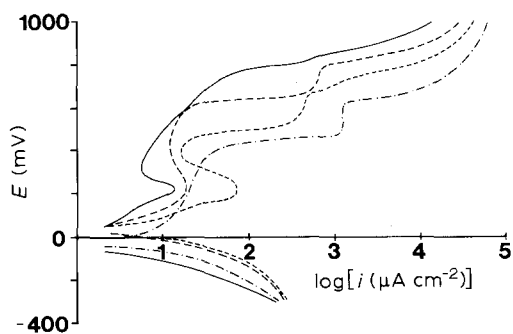
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Figure 4 Anodic potentiodynamic polarization curves of alloys (———) II-Ag, (— — —) I-Ag, (— · —) III-Ag and (— — —) III-Ag + 5 Pd in the heat-treated state.

Figure 5 Change in integrated current density Q at 700 mV for 600 s. Au–Cu–Pd: (○) homogenized, (●) heat treated. Au–Cu–Ag: (△) homogenized, (▲) heat treated.

3.2. Amount of electrochemical reaction

Fig. 5 shows the changes in Q value with nobility (total atomic fraction of Au and Pd). The Q values of alloys II, I and III were remarkably low and showed these alloys to have a high corrosion resistance. There was little difference in Q between homogenized single-phase (α_0) and heat-treated single-phase (L1$_0$).

The structures of alloys II-Ag, I-Ag and III-Ag were single-phase (α_0) in the homogenized state and were two-phase (α_1 and α_2) after heat treatment. In alloys with a nobility of less than 37 at % (I-Ag and III-Ag), the Q value of the two-phase structure was higher than that of the single-phase one, i.e. the formation of the second phase decreased the corrosion resistance. However, the alloy with a nobility of 46 at % (II-Ag) possessed a high corrosion resistance in both states.

Figure 6 Isothermal section at 300 °C of Au–Cu–Ag ternary phase diagram.

4. Discussion

All the experimental alloys have a single-phase structure of α_0 solid solution in the homogenized state. The Q values of the alloys with single-phase structure became smaller as the nobility of the alloys increased, and were constant at a nobility higher than 37 at % (Fig. 5). Anodic potentiodynamic polarization curves of the alloys with a single-phase structure indicated that the electrochemical reactions of those alloys were simple and E_c appeared at a higher potential as the nobility increased (Fig. 3).

The structures of alloys II, I and III changed from a disordered single-phase of α_0 to an ordered single phase of the L1$_0$ type on heat treatment at 300 °C. Parks et al. [12] examined the difference in the electrochemical behaviour of the ordered and disordered phases of Cu$_3$Au alloy. They reported that the E_c of the ordered alloy was 250 mV higher than that of the disordered alloy. In the alloys II, I and III, however, the effect of ordering was not clear on the potentiodynamic polarization curve (Fig. 2) and on the Q value (Fig. 5). It is considered that there is no difference in corrosion behaviour between disordered and ordered states because these alloys have a high nobility. It is reasonable to assume that the electrochemical behaviour of the single-phase alloy simply depends on its chemical composition, in other words, on the nobility of the alloy.

The alloys II-Ag, I-Ag and III-Ag have a two-phase structure consisting of α_1 and α_2 phases in the heat-
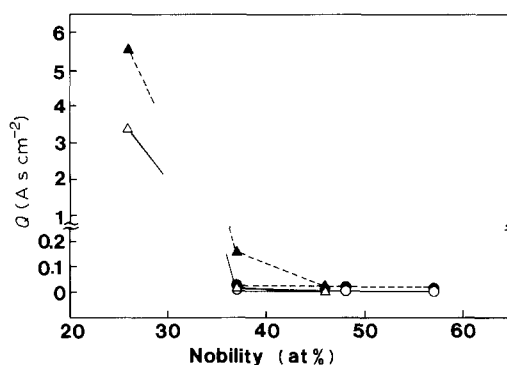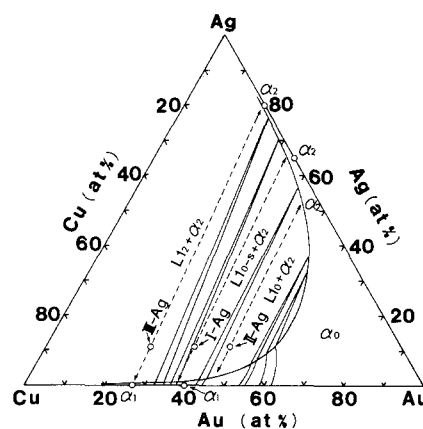
treated state. Their Q values were higher than those of the alloys with single-phase structure (Fig. 5), indicating that the corrosion was enhanced by the formation of a second phase. In the case of the high-nobility II-Ag alloy, however, corrosion resistance was unaffected because both α_1 and α_2 phases had a high gold content as shown by the Au–Cu–Ag ternary phase diagram (Fig. 6) [13, 14]. This result indicates that the corrosion resistance of the two-phase alloy depends on the composition of each phase.

In the anodic potentiodynamic polarization curve of the alloy with a two-phase structure (Fig. 4), two E_c values appeared at different potentials. It seems that each characteristic potential corresponds to the potential at which a reaction occurs in each of the two phases α_1 and α_2. The current density is thought to be related to the amount of reaction which occurs on the specimen surface, so that it should be proportional to the amount of each phase. Consequently, we assumed that the current density (i) at a given potential should be expressed as the sum of the current density of each phase by taking account of their volume fraction. That is

$$i = f_1 i_1 + f_2 i_2$$

where f is the volume fraction of a phase estimated from the phase diagram (Fig. 6). The suffixes 1 and 2 denote the α_1 and α_2 phase, respectively. To confirm this, single-phase alloys were made as duplicates of the

TABLE II Approximated compositions of the single-phase alloys

Specimen		Composition (at %)				Composition (wt %)			
		Cu	Au	Ag	Pd	Cu	Au	Ag	Pd
III-Ag	α_1	73.0	27.0			46.6	53.4		
	α_2		20.0	80.0			31.3	68.7	
I-Ag	α_1	60.0	40.0			32.6	67.4		
	α_2		35.0	65.0			49.6	50.4	
III-Ag + 5Pd	α_1	69.4	25.6		5.0	44.2	50.5		5.3
	α_2		19.0	76.0	5.0		30.0	65.7	4.3

α_1 and α_2 phases of III-Ag, I-Ag and III-(Ag + 5Pd) alloys, and were subjected to potentiodynamic polarization tests. The compositions of each phase of III-Ag and I-Ag alloys were estimated to be the composition at which the tie-line crossed the phase boundary in the isothermal section of the Cu–Au–Ag ternary phase diagram (Fig. 6). Since the solubility of silver in α_1 and that of copper in α_2 are negligibly small at room temperature, the compositions of Cu-rich α_1 and Ag-rich α_2 phases approximated to those of Cu–Au and Ag–Au binary alloys. It is impossible to estimate the compositions of the α_1 and α_2 phases of III-Ag + 5Pd alloy from the ternary phase diagram because it is a quaternary alloy. Therefore, the α_1 and α_2 phases of III-Ag + 5Pd alloy were made by adding 5 at % Pd equally to both α_1 and α_2 phases of III-Ag alloy. Approximate compositions of the single-phase alloys are shown in Table II.

Potentiodynamic polarization curves of two single-phase alloys as duplicates of α_1 and α_2 of III-Ag + 5Pd are shown in Fig. 7. The E_c of the Cu-rich α_1 single-phase alloy appeared at a higher potential than that of the Ag-rich α_2 single-phase alloy.

Measured and calculated curves for the alloys III-Ag, I-Ag and III-Ag + 5Pd are shown in Figs 8 to 10. The fit of the measured curve to the calculated one proved to be excellent. It is apparent that the higher E_c and the lower E_c correspond with the E_c of Cu-rich α_1 and Ag-rich α_2 phases, respectively, and the value of current density is expressed as the sum of the current densities of the α_1 and α_2 phases when their volume fractions are taken into consideration. This fact also indicates that there is little galvanic effect between the two phases.
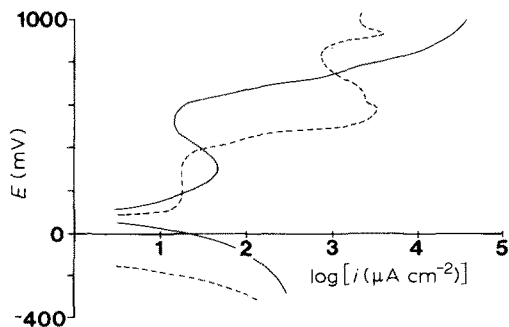

Figure 8 (———) Measured and (– – –) calculated polarization curves of two-phase heat-treated III-Ag alloy.

Figure 9 (———) Measured and (– – –) calculated polarization curves of two-phase heat-treated I-Ag alloy.

Figure 10 (———) Measured and (– – –) calculated polarization curves of two-phase heat-treated III-Ag + 5 Pd alloy.

Figure 7 Anodic potentiodynamic polarization curves of hypothetical (———) α_1 and (– – –) α_2 single-phase alloys of the III-Ag + 5 Pd alloy.
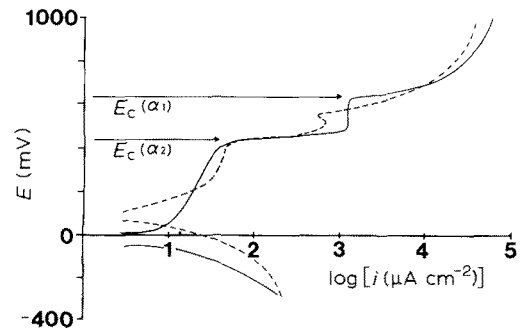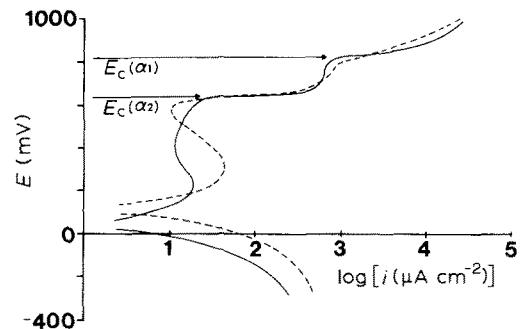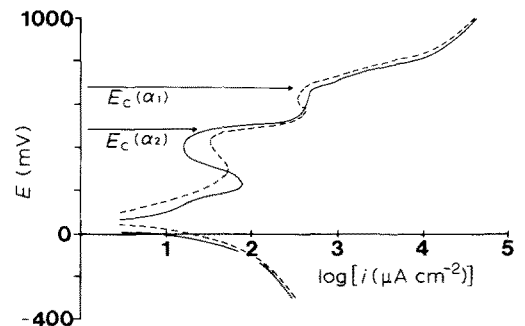
It is concluded that the complex potentiodynamic curve of an alloy with two phases can be explained by superimposing simple curves of each phase; the principle of additivity can be applied to the alloys examined in this study.

5. Conclusions

The effect of microstructure on the corrosion behaviour of Au–Cu–Pd, Au–Cu–Ag and Au–Cu–Ag–Pd alloys was studied by anodic potentiodynamic and potentiostatic polarization. The results were as follows.

1. The single-phase Au–Cu–11 at % Pd alloys high-nobility Au–Cu–11 at % Ag (46 at % Au) had a high corrosion resistance. The corrosion behaviour of those alloys was almost the same.

2. The two-phase Au–Cu–11 at % Ag and (Au–Cu–11 at % Ag) − 5Pd alloys had a lowered corrosion resistance compared with the single-phase alloys.

3. Anodic potentiodynamic polarization curves of the two-phase structure alloys were explained by superimposing the curves of each phase using the principle of additivity. The values of E_c corresponded with those of each phase, and the value of current density at each potential was calculated as the sum of the current density of each phase and taking account of volume fractions. In anodic potentiodynamic polarization, there was little galvanic effect between the two phases.

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