INTRODUCTION

Dental alloys must have a unique combination of properties. To counter mastication forces, they should have high strength and stiffness. To resist corrosive attack in the oral cavity, they should be adequately noble or corrosion-resistant. For many dental cast alloys, these critical properties are influenced by fabrication and processing variables. Unfortunately and very often inadvertently, an improvement in one property may be to the detriment of another.

A quintessential example is the dental 14-karat gold alloy. It has a complex combination of constituents comprising four or more elements; however, the key constituents are gold, silver, and copper1,2). For example, to increase alloy hardness, it could be achieved via grain interior reactions in an aging treatment. However, nodules which precipitated at the grain boundaries would result in poor corrosion resistance and a degradation of other mechanical properties.

In dental 14-karat gold alloys, age-hardening by grain interior precipitation is attributed to the development of a long-period antiphase domain structure in AuCu II type superlattice. The strain field induced by AuCu I type superlattice coexisting with AuCu II type superlattice also contributes to the age-hardening characteristic3-7). Discontinuous precipitation at the grain boundaries results in the formation of a coarse, a dual phase, lamellar structure. These phases have been identified as AuCu I type superlattice (fct) and α2-Ag solid solution (fcc)7,8).

Phase separation occurs at a certain temperature in 14-karat gold alloys. Herein lies the possibility of achieving a more homogeneous microstructure, and hence improved alloy properties, by altering the cooling rate during casting. The purpose of this research was to investigate the effect of mold temperature on the microstructure, crystal structure, and corrosion properties of a 14-karat gold alloy.

MATERIALS AND METHODS

Cast 14-karat gold alloy specimens
Chemical composition of the 14-karat gold alloy (K.14 M.C. Gold Alloy, GC Corp., Tokyo, Japan) selected for use in this research was Au-15%Ag-3%Pd-24 mass%Cu. Disk-shaped alloy specimens (1.3 mm thickness and 9 mm diameter; n=3/group) were produced by lost wax casting under an argon atmosphere with an aspiration pressure casting machine.

During casting, mold temperature was set at 22, 250, 400, or 700°C (manufacturer-recommended temperature). Gold alloy specimens produced using each corresponding mold temperature were assigned accordingly into alloy groups abbreviated as 22T, 250T, 400T, or 700T. For another alloy group “sol”, specimens were cast using a mold temperature of 700°C and then solution heat treated for 1 h at 800°C in a vacuum. This was followed by rapid cooling in ice water. Cooling curves were generated during the casting procedure by measuring the temperature with thermocouples (0.2 mm diameter; n=3/group) already embedded in the disk wax pattern.

Cast specimens were ground with silicon carbide paper (600-grit) and metallographically polished to a mirror-like finish using alumina paste (5.0 μm and 0.3 μm).
Scanning electron microscopy (SEM)
Polished specimens were etched for 10 s using 20% ammonium peroxydisulfate and 20% potassium cyanide. SEM (X-650, Hitachi, Tokyo, Japan) micrographs were taken at 100–400× magnification and then compared qualitatively and quantitatively. Quantitative measurement referred to digitally measuring the area fraction of nodules contained in the microstructure in micrographs taken at 400× magnification.

Potentiodynamic polarization scanning
Potentiodynamic polarization scanning of the gold alloy specimens was conducted in a pH 7.4 physiological salt solution (0.9% NaCl, 1% lactic acid, 4% sodium hydroxide; total volume: 1,000 mL) maintained at 37°C. Using a potentiostat (Model HZ-1A, Hokuto Denko Corp., Tokyo, Japan), each specimen’s current density was measured at a scan rate of 1 mV/s in the potential region of −200 to +1,200 mV (vs. Ag/AgCl reference electrode).

X-ray diffraction (XRD) analysis
A micro XRD unit (RINT-2500, Rigaku Corp., Tokyo, Japan) using Ni-filtered CuKα radiation (40 kV tube voltage and 200 mA current) was used for XRD analysis of the gold alloy specimens. Scans were conducted at 2°/min over a 2θ range of 30° to 90°.

RESULTS AND DISCUSSION

Cooling curves of molten alloys
Figure 1 shows the cooling curves of the alloy specimens from casting temperature to 200°C. Cooling rate was calculated as being approximately the slope of the straight line between maximum temperature after casting and 200°C on the cooling curve. The cooling rates were approximately 760°C/min, 43°C/min, 22°C/min, and 18°C/min for 22T, 250T, 400T, and 700T respectively. The cooling rate for 22T was nearly 40 times higher than that of 700T, reaching a temperature of 200°C within 52 s. The slopes of the cooling curves of 250T and 400T became more gradual at temperatures lower than 500°C, hence resulting in slower cooling rates.

Microstructure observation via SEM
Figure 2 displays the microstructures of the following alloy specimens: (a) solution heat treatment; (b) 22T; (c) 250T; (d) 400T; (e) 700T.
With 14-karat gold alloy, grain boundary precipitates (nodules) exist as two phases: AuCu I superlattice (fct) and $\alpha_2$-Ag solid solution (fcc). In the solution heat treatment group, no nodule formation was observed. In the 22T group, hardly any nodules were formed. In other words, specimens in solution heat treatment and 22T groups exhibited single-phase microstructures. In 250T (Fig. 2c), only a small number of nodules were formed at grain boundaries, and this was markedly reduced compared to 400T (Fig. 2d) and 700T (Fig. 2e). Interestingly, nodule formation was greater in 400T than in 700T, although the time available for diffusion, which is needed for nodule formation, was shorter for 400T.

**Area fractions of nodules**

Figure 3 shows the digitally measured area fractions of nodules in the microstructure of each alloy group. Consistent with the qualitative observation of the microstructures presented above, the area fraction of nodules in 400T was pronouncedly higher than that of 250T. However, further increase in mold temperature did not result in continued increase in nodule formation, since the area fraction of nodules in 700T was less than that in 400T. Thus, 400T exhibited the greatest area fraction of nodules. In sharp contrast, there was practically no nodule formation in 22T (<1% or ɛ<0.01). As for 250T, its area fraction of nodules was significantly lower than that of conventional 700T.

**Potentiodynamic polarization curves**

Figure 4 shows the potentiodynamic polarization curve of each alloy group. The solution heat treatment, 22T, and 250T alloy groups exhibited greater, or more noble, corrosion potentials ($E_{corr}$) than 400T and 700T. Among these groups, the solution heat treatment group was slightly more noble than 250T; similarly, 700T was slightly more noble than 400T. Within the same alloy system, a specimen which has a more noble corrosion potential has greater corrosion resistance. Therefore, 22T and 250T alloys should have improved corrosion resistance compared to the 700T alloy (cast at manufacturer-recommended mold temperature). This meant that when casting this 14-karat gold alloy, the use of mold temperatures at 250°C or below would improve corrosion resistance. Alternatively, if mold temperature were set at 700°C, solution heat treatment would also significantly improve corrosion resistance since the corrosion potential of solution heat treated alloy was greater than that of 700T.

The potentiodynamic polarization results were in good correlation with SEM analysis (Fig. 2) and nodule area fraction measurement (Fig. 3) results. Solution heat treated and 22T alloys exhibited no observable grain boundary precipitates and were thus single phase. Conversely, 400T and 700T alloys contained an abundance of grain boundary precipitates or nodules, indicating that additional phases and structures were introduced into their microstructures. Taken together, these results implied that a more complex microstructure would negatively impact corrosion properties.

According to the mixed potential theory, corrosion potential could be viewed as a weighted sum of the individual potentials of constituents. The nodules or precipitates were clearly more anodic, hence depressing the overall potential of the alloy when they were present. For this reason, 400T and 700T exhibited lower corrosion potentials than 250T and 22T. Besides, if the nodules were present in greater abundance, e.g., 400T had more nodules than 700T, 400T displayed a lower corrosion potential than 700T. Amongst the more noble alloys, it was not surprising that the corrosion potential of solution heat treated alloy was slightly more noble than the 22T and 250T alloys because of the effect of homogenization heat treatment.

**XRD spectra**

Figure 5 displays the X-ray diffraction spectrum of each alloy. Solution heat treatment and 22T groups exhibited similar spectra with only the $\alpha$ phase (fcc) present. Casting at mold temperature of 400 or 700°C resulted in specimens possessing both $\alpha_2$-Ag solid solution and...
AuCu I (fct) crystalline phases, as well as markedly less α phase than solution heat treatment and 22T groups. Although the pseudo-binary phase diagram of AuCu-Ag system (Fig. 6) predicted equilibrium phases of α2-Ag solid solution and AuCu II phases at low temperatures, the phases observed by XRD were α2-Ag solid solution and AuCu I phases. Besides, the (111) peak of α2-Ag solid solution and AuCu I phase for 400T was sharper than that of 700T (Fig. 5). This indicated a more accelerated phase separation reaction in 400T than in 700T, which was consistent with SEM (Fig. 2) and nodule area fraction measurement (Fig. 3) results. Focusing on the high-angle side, a broadening of the peaks was observed in 250T, 400T, and 700T, indicating the progress of hardening by an order-disorder transformation8).

Reason for reduced nodule formation in 700T than in 400T
As the mold temperature increased from 22°C to 250°C and 400°C, so did the amount of nodules observed in the 14-karat gold alloy. Curiously, 700T alloy exhibited fewer nodules compared to 400T alloy. Referring to the pseudo-binary equilibrium phase diagram of AuCu-Ag system9) in Fig. 6, the straight, vertical, dashed line indicates the chemical composition of the alloy used in this experiment. I and II represent the AuCu I and AuCu II phases respectively. Phase separation reaction from α-solid solution to α1-Cu solid solution and α2-Ag solid solution occurred at about 540–550°C. Due to very rapid cooling rates, the solution heat treated alloy (which was cooled in ice water) and 22T alloy retained the α-solid solution phase, which is typically stable at high temperatures. For 250T, phase separation reaction, which is characterized by nodular formation, did not occur at 540–550°C. This was because the cooling rate of 250T (Fig. 1) was very rapid until below 400°C, at which point its cooling rate slowed down.

400T alloy exhibited a higher degree of nodule formation than 700T alloy (Figs. 2 and 3). This reverse phenomenon could be explained on two fronts: grain growth of the α phase reduced grain boundary energy (kinetic energy) and changed the solute concentration of the supersaturated solid solution (chemical driving force). The cooling rate of 700T slowed down as it reached 700°C (Fig. 1). Thus, 700T probably underwent grain growth as it remained a supersaturated solid solution until it reached a temperature of about 540°C. Thereafter, grain interior and phase separation reactions proceeded10,11). Conversely in 400T, it was probable that both active grain growth and phase separation reaction occurred simultaneously, resulting in comparatively increased nodule formation as the cooling rate slowed down around 500°C (Fig. 1).

CONCLUSIONS
Within the limitations of the current study, the following conclusions were drawn:
1. Nodule formation was suppressed in the 14-karat gold alloy when cast using mold temperatures of 250°C or below.
2. For the alloy cast at mold temperature of 700°C, solution heat treatment for 1 h at 800°C in a vacuum caused the nodules to disappear.
3. Corrosion potentials of the alloys cast at mold temperatures of 250°C or below were more noble than the alloy cast using the conventional mold temperature of 700°C, indicating improved corrosion resistance.
4. Two factors influenced nodule formation: cooling rate and the temperature at which cooling rate slowed down. For the alloy cast using a mold temperature of 250°C, its cooling rate slowed down below 400°C, retarding grain boundary and phase separation reactions. For the alloy cast using a mold temperature of 400°C, its cooling rate slowed down around 500°C, allowing phase separation and nodule formation to simultaneously occur in abundance.
REFERENCES


