

A binary dental gold-cobalt alloy of eutectic composition

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A new dental gold alloy was investigated for the casting of prosthetic restorations. The binary alloy is composed of 10 weight-percent Co and 90 wt% Au. Studies of the structure of the alloy revealed a rod-eutectic structure with Co rods in Au matrix. By special heat treatment (solution treatment and precipitation treatment) the hardness was increased up to 280 Hv. The hardening effect caused by Co atom groups in the Au matrix was studied by transmission microscopy. Casting experiments were performed using conventional dental casting procedures. Metallographic studies revealed no Co rods in the surface layer of the castings after the heat treatment. □ *Dental materials; ultrastructure; hardness*

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The composition of dental casting alloys is at present of a very complex nature. The complexity has been increased to obtain better physical properties. The number of added elements has gradually increased from a few to about nine components. This is especially valid for ceramic alloys. Segregation can be developed when the differences between solidus and liquidus temperature of the alloy is large. Differences in concentration may exist within the grain (microsegregation) and

also between large regions in the structure (macrosegregation). These inhomogeneities of the alloy will impair the corrosion resistance and physical properties (4). For these reasons it may be desirable to reduce the number of elements in a dental casting alloy to as few as possible. Whereas pure gold is too soft as a casting metal, a binary alloy will be close to ideal.

Eutectic alloys are generally known to be good casting alloys, because of their lack of

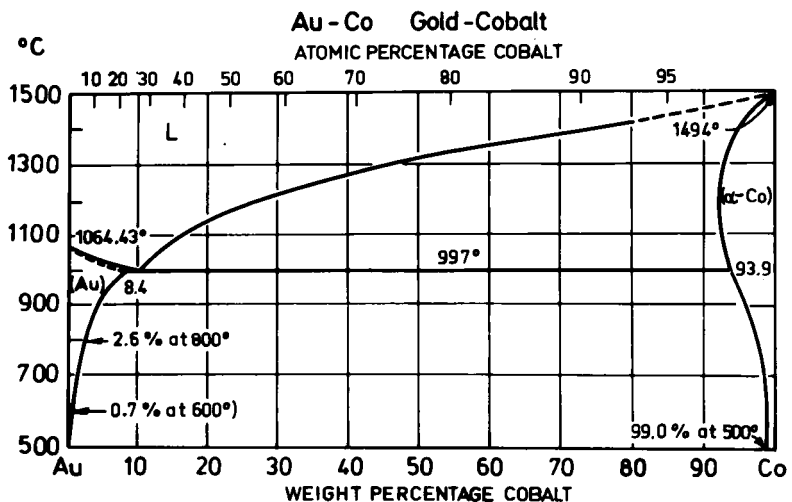


Fig. 1. The phase diagram Au-Co.

solidification interval and the lowest melting temperature in the alloy system. Castings of such alloys are characterized by low risk of pores and cracks. They solidify mostly without forming ordinary grain structure.

An advantageous casting alloy for dental applications will, because of these reasons, be a binary eutectic alloy, in which two elements solidify at the same temperature without segregation.

The aim of this investigation was to develop a binary, eutectic gold alloy to be used as a casting alloy for prosthodontic reconstructions and to study the mechanical properties by hardness tests and by metallographic and electronmicroscopic studies.

Material

The Au-Co phase diagram (Fig. 1) has an eutectic point at 10 weight-percent Co and 90 weight-percent Au (1). The phase diagram also indicates the possibility of precipitation hardening. The eutectic structure of this system was described by Sahm & Killias (5) in unidirectionally solidified materials. The binary Au-Co system has previously been discussed because of the hardening potential (6).

A study of the hypoeutectic Au-Co alloys was performed by Gettleman et al. (2). With a low percentage of Co an increasing age hardening effect was observed with increasing percentage of Co, as expected from the phase diagram. However, the eutectic alloy was not studied and not described in the literature as a dental gold casting alloy. The purpose of this study was to investigate the Au-Co system at the eutectic point (10 weight-percent Co) and to evaluate the hardening effect of the precipitation treatment.

Experiments

In a preliminary study Au and Co were alloyed in five different weight-percent compositions (4, 6, 8, 10, and 15 wt% Co) to establish the eutectic point and to investigate

the metallography of alloys with a composition close to the eutectic range.

The melting was carried out in an induction-tube furnace in Ar-gas. The alloy was kept melted for 5 min for homogenization and subsequently solidified in Ar-gas.

Samples of 3 g of the castings were solution-treated in Ar-gas at a temperature of 950°C for 15 min and immediately quenched in water. After the solution treatment samples were hardened by precipitation treatment. Hypothetically, it was assumed that a temperature of 100–500°C for 15, 30, and 60 min, respectively, was suitable. On the basis of these experiments subsequent solution treatment was conducted at a temperature range of 800–950°C for 15 min and a precipitation hardening at a temperature of 200–400°C for 15 min.

Metallographic investigation

The specimens were prepared according to routine methods. Etching was performed in aqua regia. Microscopical investigation was carried out in a Zeiss-III photomicroscope and Wild-400 photomicroscope.

The hardness of the alloy

The Vickers hardness was tested on each specimen by ten indentations with a load of 5 kp. Measurements were made after casting and after solution treatment and precipitation hardening.

Electronmicroscopic investigation

Electronmicroscope studies were performed in a transmission-electron-microscope (TEM, Jeol-1MV-1000D). The specimens were prepared with an ion-beam thinning machine (Technics) to facilitate the transmission studies in solution-treated and precipitation-hardened samples.

Casting tests

The binary eutectic alloy with a melting temperature of 997°C was cast (Heraeus casting machine, type no. Cl-G) to test casting properties of the alloy. The temperature of



Fig. 2. The blade-edge test casting.

the invest material was about 600°C. Two different tests were performed. One full crown restoration of a posterior tooth and one blade-edge test casting were cast. The latter one was cast to analyze the casting

fluidity and mould filling properties of the alloy (Fig. 2). The casting tests performed showed satisfactory properties in reproducing the investment mould and fitness to the mould.

The cast restoration was solution-treated at 950°C for 15 min and precipitation-hardened at 300°C for 15 min in argon gas. The full crown was then polished in a normal way. The inlet and the full crown restoration were divided into two parts.

Results

Metallographic study

Five Au-Co alloys with various weight-percentages of Co (4, 6, 8, 10, and 15 wt %) were studied. Fig. 3 demonstrates the structure in the alloy with 8 wt % Co. Primary solidification of Au-rich dendrites with a rod-eutectic structure between the dendrites can be observed. Inside the dendrites a plate-like precipitation of Co can be seen. Those plates have precipitated in solid state during the cooling. All the alloys between 4 and 8 wt % showed the same type of structure. The fraction of the eutectic structure, however, increased with increasing Co content.

The eutectic alloy (10 wt % Co) demonstrated a normal composite eutectic structure with a uniform eutectic cell structure consisting of a gold matrix with Co rods (Fig.

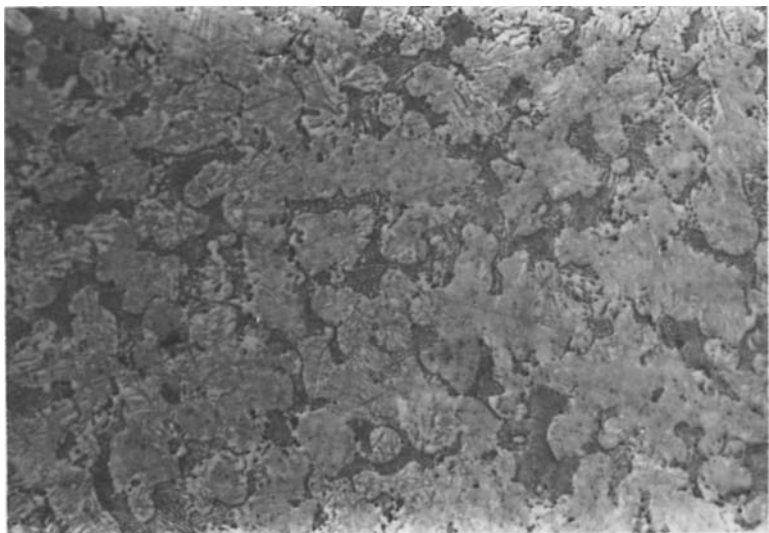


Fig. 3. The microstructure of the cast alloy with 8 weight-percent Co. ($\times 200$.)

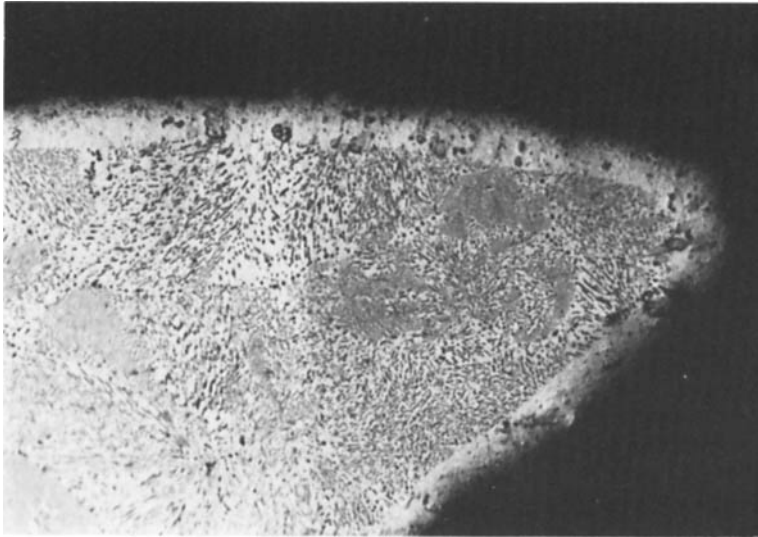


Fig. 4. Cast crown. A thin layer of Au matrix covers the surface. The Co rods have different directions in each unit cell. ($\times 290$.)

4). The thickness of the rods and the distances between them varied with the cooling rate. The rod thickness was estimated to be less than $0.1 \mu\text{m}$, and the distance between them was calculated to be $1 \mu\text{m}$. The alloy of 15 wt % was characterized by a primary precipitation of $\alpha\text{-Co}$ as dendrites and the

remaining melt solidified into a eutectic structure.

Hardness test

The metallographic study exhibited a eutectic structure without defects. No Co

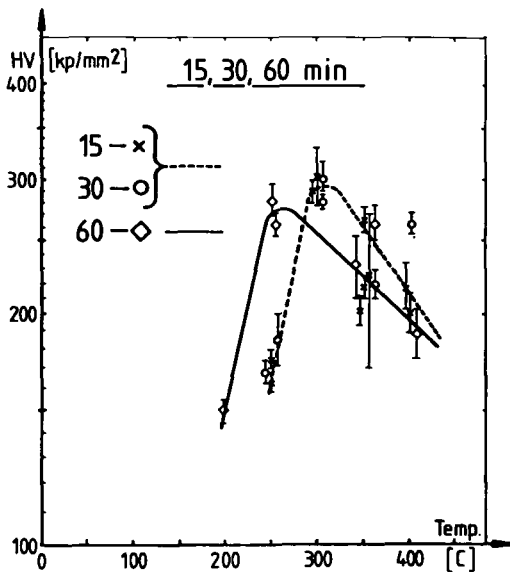


Fig. 5. The hardness (Hv) as a function of the precipitation-hardening temperature at different times. Solution treatment, 950°C .

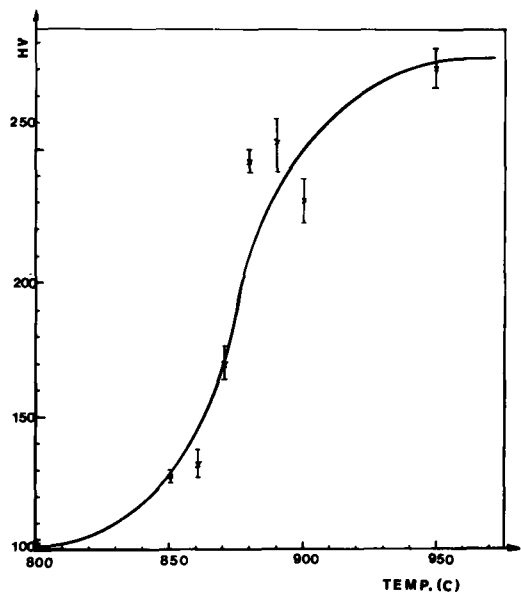


Fig. 6. The hardness (Hv) as function of the solution temperature at a precipitation hardening temperature of 300°C for 30 min.

rods were observed on the surface layer (0.1 mm). The hardness test was performed on the eutectic alloy before and after solution treatment and after precipitation hardening. Both the cast alloy and the solution-treated alloy had a hardness of about 100 Hv. The results from the experiments with a solution temperature of 950°C and precipitation hardening at different temperatures and times are plotted in Fig. 5. The data from measurements after age-hardening for 15 and 30 min were equivalent and displayed a hardness maximum of about 280 Hv at a temperature of 300°C. The hardness curve of 60 min precipitation hardening revealed a maximum hardness value of about 260 Hv at 250°C. Fig. 6 shows the hardness as a function of the solution temperature in samples precipitation-hardened at 300°C. The figure shows a sharp drop in hardness when the solution temperature decreased from 900°C to 850°C. A solution temperature above 900°C gave only a marginal increase

in the hardness, whereas a temperature of 875°C resulted in lower hardness values for the same precipitation conditions. By increasing precipitation temperature and time, this hardness reduction can be compensated (Fig. 7).

Electron microscope studies

The transmission electron microscope studies of the two samples revealed two different structures. The solution-treated specimen revealed no Co particles in the Au matrix between the Co rods. The precipitation-hardened sample showed a large amount of Co-rich particles in the Au matrix (Fig. 8). The two semicircles of the aggregates indicate a possible coherence between particles and matrix.

Discussion

The metallographic investigation showed a binary lamellar eutectic composite, which solidified into a typical cell structure without segregation. The lamellars were alternating Au- and Co-rich without intermediate phases in each other.

The casting trials performed resulted in dental casting with good reproduction of details and low pore formation, which is to be expected in solidified eutectic alloys.

The solution treatment of the alloy will give a rather even concentration of Co atoms throughout the whole matrix. The Co atoms will not, however, substantially strengthen the Au matrix, as indicated by the hardness measurements. After age-hardening, precipitates are formed. The precipitation-hardening process was controlled by the time and temperature of the process. The maximal hardness was obtained at 300°C for 15 min. Fig. 8 shows a TEM structure of an age-hardened alloy. It was difficult to make a diffraction pattern on the precipitates, but it will be assumed that those precipitates consist of α -Co. The precipitates grew to a maximum size of 25 Å at the optimal hardened condition.

Co has been observed to precipitate in an FCC gitter (3) ($a = 3.54 \text{ \AA}$). The gitter par-

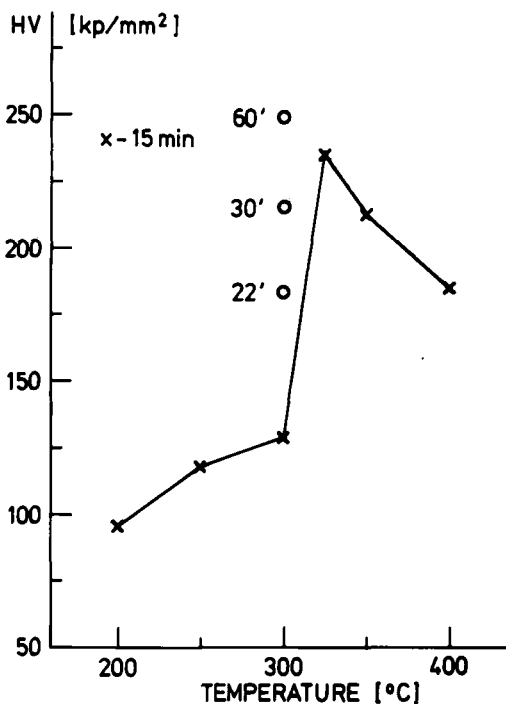


Fig. 7. The hardness (Hv) as a function of the precipitation-hardening temperature at different times. Solution treatment, 875°C.



Fig. 8. The transmission electron microscopic structure of the precipitation-hardened alloy (300°C, 15 min). Coherence pattern, Co particles of different sizes. (30–50 Å, $\times 300,000$.)

ameter of Au (FCC) has been found to be 4.07 Å. A discrepancy between these parameters can be calculated to be about 14%. The Co particles and the matrix may therefore be semicoherent, as indicated by the TEM micrograph (Fig. 8), and significantly to the increased hardness. However, owing to the rather large misfit, the semicoherency can only exist as long as the particles are small enough. No TEM studies were made on plastically deformed materials.

The heat treatment of the samples—solution treatment and precipitation hardening—revealed the possibility of increasing the hardness from 100 Hv to 280 Hv. However, there are possibilities for obtaining hardness values between these two limits, which may increase the clinical application of the alloy within the dental field.

Two ways can be selected here with the help of Figs. 5 and 6: either a solution treatment at a temperature of 900–950°C and a

precipitation hardening at a temperature above 300°C or a solution treatment at a temperature between 850°C and 900°C and precipitation hardening at 300°C (Fig. 7). In the first case the coarseness of the precipitated Co particles determines the hardness and can be varied by selecting an appropriate precipitation-hardening temperature. In the second case the hardness is determined by the number and size of Co particles precipitated during the precipitation hardening. The number of particles is affected by the amount of Co in the Au matrix before the precipitation hardening, which is determined by the solution temperature and the equilibrium solubility of Co in the Au matrix. The large rise of the hardness curve in Fig. 6 between 850°C and 900°C indicates a large increase of hardness with increasing temperature of solution treatment. In comparison, the slope of the precipitation-hardening curve (Fig. 5) indi-

cates a more moderate hardness decrease with increasing temperature, which enhances the possibility to obtain the desired hardness value in the range of 150–200 Hv. This hardness range was chosen because an alloy with a hardness greater than 200 Hv will be very brittle and an alloy with a hardness below 150 Hv will be too soft.

After the heat treatment no Co rods were observed in the surface layer. The thin Co-free layer of the surface might depend on a slight oxidation of Co during the heat treatment due to a too high oxygen potential in the protecting atmosphere. A thin oxide layer could also be observed on the heat-treated samples. This oxide layer is removed during the following technical procedures of the crown restoration.

Conclusions

A binary eutectic Au–Co alloy composite has been tested for the casting of dental

prosthetic restorations. The alloy exhibited appropriate casting properties and can be precipitation hardened up to 280 Hv.

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