Phase transformation in a dental Pd–Cu–Ga alloy

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Abstract

Phase transformation behavior in a dental Pd–Cu–Ga alloy was studied by means of hardness tests, electrical resistivity measurements, X-ray diffraction and transmission electron microscopy. Annealing at 673 K produces two hardness peaks which correspond to the formation of a metastable phase with ordered fct structure and the precipitation of the equilibrium phases, α_1(fcc) + α_2(fcc) + Pd_2Ga (orthorhombic), respectively. On the other hand, annealing at 873 K exhibits only one peak due to the precipitation of the equilibrium phases. The difference of the phase transformation between both annealings is interpreted in terms of the free energy.

Keywords: Phase transformation; Pd–Cu–Ga alloy; X-ray diffraction; Age-hardening; Transmission electron microscopy

1. Introduction

For the dental porcelain-fused technique, palladium-base alloys have taken over gold-base alloys without fully understanding the qualities because of the suddenly price rise in gold in 1980. Especially, there is a lack of information about the strengthening, though it is well known that most porcelain-fused metals are age-hardenable and the age-hardening has been utilized to acquire the required strength. A few papers [1–3] have been concerned with the phase change in the Pd–Cu–Ga ternary system regardless of dental use. Reiff [1] first investigated a Pd–10 mass%Cu–10 mass%Ga alloy, which had very high strength with a fibrous structure after deformation and annealing at 653 K. Thereafter, Khabliyev et al. [2] and Odén and Herø [3] intended to elucidate the phase transformation and the hardening mechanisms in Pd–Cu–Ga alloys. However, they have been insufficiently understood up to date. This understanding becomes more important because such high-palladium alloys for application of porcelain fused to metal have shown satisfactory corrosion resistance in an oral environment [4,5].

In order to ascertain the aging reactions and the hardening mechanisms, the present work was performed on a dental Pd–Cu–Ga alloy with composition similar to those in Refs. [1–3] using hardness tests, resistivity measurements, X-ray diffraction (XRD), and transmission electron microscopy (TEM).

2. Experimental details

The specimen used in this work was a dental porcelain-fused alloy with 81.9 mass%Pd–8 mass%Cu–7 mass%Ga–3.1 mass%X (AURORA, Shofu Inc., Kyoto, Japan). The X refers to the unpublished elements.

Sheets of 0.5 mm and 0.1 mm thick were prepared by alternate rolling and annealing for the hardness tests and for other experiments, respectively. These specimens were solution-treated at 1173 K for 3.6 ks under an argon atmosphere and then quenched into ice brine. Subsequently, anisothermal annealing at the heating rate of 16.7, 8.33, 4.16 or 1.67 mK s^{-1} (1, 0.5, 0.25 or 0.1°C min^{-1}) from room temperature to 1173 K in vacuo, and isothermal annealing at 673, 773 or 873 K were carried out.

The hardness tests were made using a Vickers hardness indenter with a 0.98 N load. The resistivity measurements were made using a d.c. potentiometric method with four probes. The structural changes were examined with XRD and TEM. For the XRD, minus-

300 mesh powder was prepared from the alloy by filing. The powder specimens in an evacuated silica tube were solution-treated and aged. An X-ray diffractometer (RAD-rA, Rigaku Corp., Tokyo, Japan) was employed using nickel-filtered Cu Kα radiation with 50 kV and 150 mA. For the TEM, discs of 3 mm diameter were punched out of the heat-treated sheets. They were electrothinned by a double-jet technique. The electrolyte used was 20% perchloric acid in acetic anhydride. The TEM observations were performed at 200 kV (H-800, Hitachi Co., Tokyo, Japan).

3. Results and discussion

3.1. Anisothermal annealing

Fig. 1(a) shows variations of resistivity with temperature in the solution-treated alloy during continuous heating (O) and subsequently continuous cooling (●) at a rate of 4.16 mK s^{-1}. Upon heating the resistivity begins to decrease at about 500 K. After attaining a bottom, it increases again, followed by two small changes in slope at about 800 K and 1040 K. The latter is shown in an inset because of the much smaller change. Subsequent cooling produces a change of the slope at about 920 K. The behaviors can be seen more clearly on the $d\rho/dT-T$ curve as shown in Fig. 1(b). These changes suggest that some phase transformations in the present alloy occur in three stages (I, II and III) during the heating and in one stage (reverse III) during the cooling. Though the data with other heating rates are not shown in this figure, a heating-rate dependency for each reaction was observed. Using the temperatures of maximum reaction rate on each heating scan, a Kissinger plot [6] was constructed for each stage and good straight lines were obtained

Fig. 2. Kissinger plots for stages I, II and III, where T_m and T_f denote the temperature of the maximum reaction rate and the heating rate, respectively.

(Fig. 2). The calculated activation energies are 201 kJ mol^{-1}, 270 kJ mol^{-1} and 287 kJ mol^{-1} for the stages I, II and III, respectively. Unfortunately, we could not estimate each elemental process from the activation energies because of lack of any diffusion data.

Fig. 3 shows a sequence of phase transformations by XRD for the specimen during continuous heating. After a heating rate of 4.16 mK s^{-1} to each temperature indicated in the figure, the specimen was quenched and an XRD scan was performed at room temperature. As can be seen in Fig. 3, the following phase changes were recognized:

$$\alpha_0(\text{fcc}) \xrightarrow{\text{I}} \beta(\text{fct}) \xrightarrow{\text{II}} \alpha_1(\text{fcc}) + \alpha_2(\text{fcc}) + Pd_2Ga \text{ (orthorhombic)}$$
$$\xrightarrow{\text{III}}$$

During heating to 623 K, there is no new peak in the XRD profile though a main reaction occurs as can be seen by a large decrease of the resistivity in Fig. 1. However, the lattice constant of the α_0 matrix decreased slightly. This fact suggests that a precipitation occurs in the specimen as pointed out by Krawits and
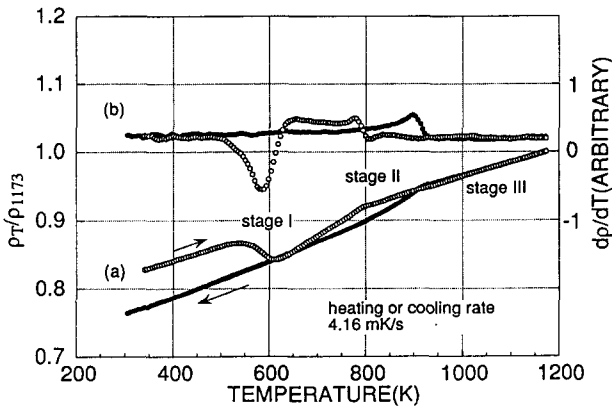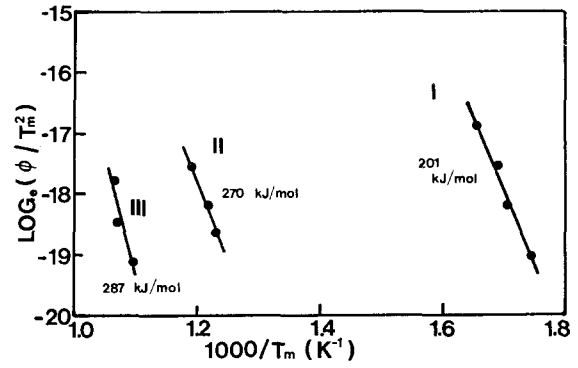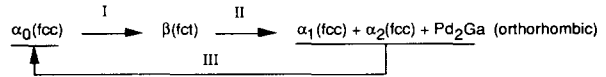

Fig. 1. Variations of resistivity (a) and their temperature derivatives (b) in a Pd-Cu-Ga alloy during continuous heating or cooling at a rate of 4.16 mK s^{-1}. An inset indicates an enlargement of the resistivity (O) and its derivatives (△) in the vicinity of stage III during heating.
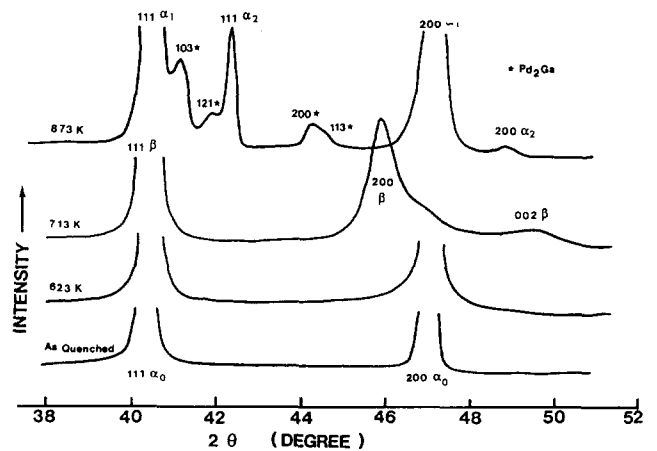

Fig. 3. Set of X-ray diffraction profiles of a Pd-Cu-Ga alloy during continuous heating of 4.16 mK s^{-1}.

Sinclair [7]. It is considered from the data at 713 K that the precipitate must be a face-centered tetragonal (fct) β phase with the $L1_0$ structure. At 873 K the lattice parameters of the reaction products, $\alpha_1 + \alpha_2 + Pd_2Ga$ are almost the same as those in the slow-cooled specimen. Therefore, it is thought that stage II corresponds to a reaction forming the equilibrium phases.
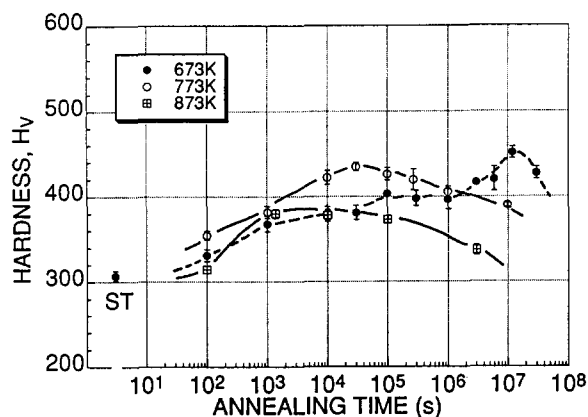

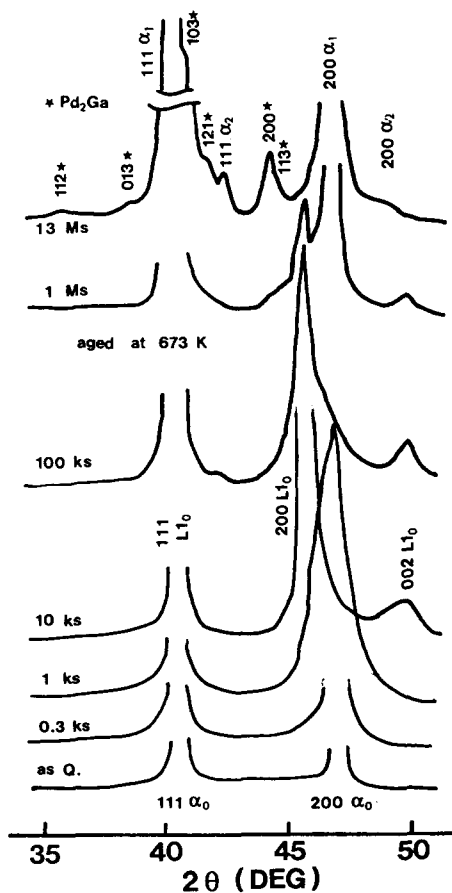Fig. 4. Hardening curves in a Pd–Cu–Ga alloy annealed at 673, 773 or 873 K.

Fig. 5. Set of X-ray diffraction profiles of a Pd–Cu–Ga alloy annealed at 673 K for various times.

Anyhow, the phase transformation process to the equilibria during the anisothermal annealing bear analogy to those during the isothermal annealing at lower temperature (673 K), which will be shown in Section 3.3.

3.2. Hardening behavior

Results of the hardness tests are shown in Fig. 4. The hardening characteristics at 673 K are different from those at 773 K or 873 K. The former gives rise to two peaks in the hardness curve, while the latter reveal only one. However, it is obvious from the results in Sections 3.3 and 3.4 that the equilibrium phases at both temperature ranges are the same. It will be discussed in a Section 3.5 why different stages are produced in the present alloy.

3.3. Aging behavior at 673 K

Fig. 5 shows a set of XRD profiles of the Pd–Cu–Ga alloy annealed at 673 K for various times. A two-step phase change is detected as follows;

$$\alpha_0(fcc) \rightarrow \beta(fct) \rightarrow \alpha_1(fcc) + \alpha_2(fcc) + Pd_2Ga$$
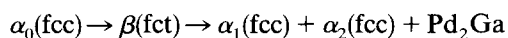
With increasing aging time, the α_0 phase with a face-centered cubic (fcc) structure transforms to three phases, which correspond to the equilibrium phases, via a metastable β phase with an fct structure ($L1_0$), the axial ratio of which is about 0.93 ($a = 0.3958$ nm, $c = 0.3680$ nm). This fct phase cannot be expected in the Pd–Cu–Ga ternary system judging from the previous data [8] in each binary alloy. However, Schubert and coworkers [9,10] have reported the existence of tetragonal and orthorhombic structures in Pt_2Ga and Pt_2CuGa. Considering Pd to be in platinum group, it may be possible that Pd_2Ga also has a tetragonal structure. When comparing this phase change with the hardening behavior at 673 K, as seen in Fig. 4, two kinds of reactions must contribute to the respective hardening. At the aging for 1 ks, the 200 line of the α_0 phase expands considerably. This is attributed to the appearance of tetragonal distortions, judging from the XRD data of further annealings. Fig. 6 shows dark-field (DF) images (Figs. 6(a) and 6(b)), corresponding selected-area diffraction (SAD) (Fig. 6(c)) and its key diagram (Fig. 6(d)) taken from the specimen aged at 673 K for 1 ks. Though the superlattice spots are very weak, analysis of the SAD pattern proves the appearance of the fct β phase ($L1_0$) with three c-axis variants, which have been reported in dental gold alloys by Kanzawa et al. [11] and Hisatsune et al. [12]. The DF images as seen in Figs. 6(a) and 6(b), are almost similar to theirs. Figs. 6(a) and 6(b) correspond to the image taken from the 202_X and 220_Z spots, respectively.
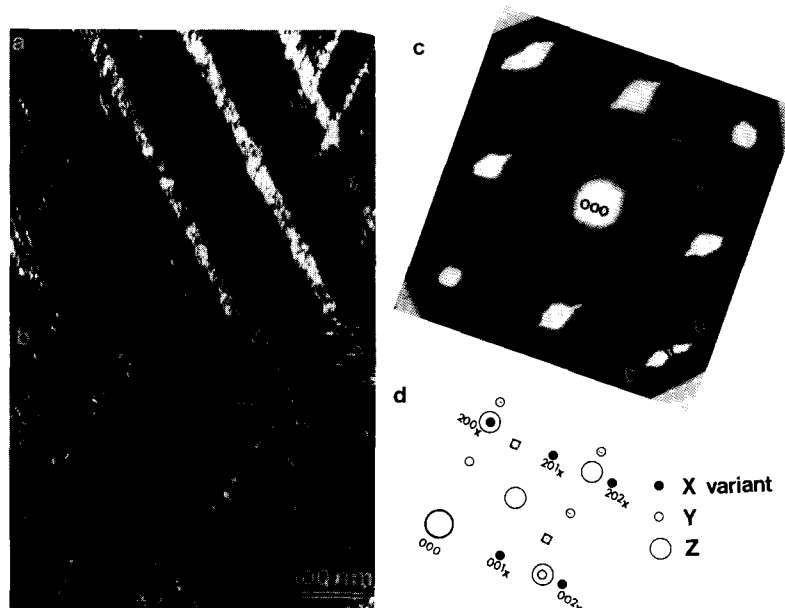
Fig. 6. The 202_X (a) and 220_Y (b) DF images, and the corresponding (001) SAD pattern (c) and its key diagram (d) of a Pd–Cu–Ga alloy aged at 673 K for 1 ks. Subscripts X, Y and Z refer to the direction of the c axis in the β phase. Extra spots shown by arrows in (c) and by open squares in (d) were produced from the intersection of extended $\langle 110 \rangle$ streaks.

Subscripts X, Y and Z refer to the direction of the c axis in the β phase. It is clear that the formation of very fine platelets is associated with the age-hardening of this alloy as seen in Fig. 4. Each spot extends into streaks along the $\langle 110 \rangle$ direction perpendicular to the thin laths which were reported by Odén and Herø [3]. It is to be noted that there are extra spots shown by arrows in Fig. 6(c) and by open squares in Fig. 6(d). As reported by Tanner [13] in a Cu–Be alloy, we can consider that these extra spots were produced from the intersection of extended $\langle 110 \rangle$ streaks mentioned above. Both Khabliyev et al. [2] and Odén and Herø [3] reported a coexistence of two different fct phases as metastable phases that had been produced during annealing in a Pd–Cu–Ga alloy with similar composition. Hisatsune et al. [12] have reported a coexistence of two distinguishable CuAu I (fct) phases with an $L1_0$ structure in a low-gold dental alloy. However, one of them was stable and the other was unstable. It is very curious that two fct structures exist in such a simple alloy Pd–Cu–Ga. We can evaluate fairly well the occurrence of the first fct phase, while it is surmised that Khabliyev et al. [2] misidentified the second fct phase. In their Fig. 3, there is no splitting of the 220 reflection, which should be separated into 220 and 202 from the existence of an $L1_0$ phase. From their XRD profiles, the phase should be identified as an fcc phase, which corresponds to the matrix phase. Odén and Herø [3] concluded that two fct phases are ordered with a difference in the c/a ratio from the existence of two separate forbidden 110 reflections on the SAD pattern. One of them may be a misunderstanding from

the suggestion of Khabliyev et al. [2]. A second reflection near the 110 position may be due to the existence of Pd_2Ga with a rhombic structure as mentioned below.

The precipitate phase in the second stage has an orthorhombic structure like that of a Pd_2Ga compound but the lattice parameters are slightly less, $a = 0.4098$, $b = 0.5359$, $c = 0.7777$ nm as compared with $a = 0.4064$, $b = 0.5493$ and $c = 0.7814$ nm for Pd_2Ga [14]. Some copper atoms may be included in the compound. Odén and Herø [3] speculated the existence of a compound Pd_3Ga with an $L1_2$ structure but we did not find this phase in our specimen.

3.4. Aging behavior at 873 K

Fig. 7 shows a set of XRD profiles of the Pd–Cu–Ga alloy during an isothermal annealing at 873 K. A short annealing for 0.3 ks produces new reflections as shown by arrows, while further annealing increases their intensity. Finally three phases are identified as α_1(fcc), α_2(fcc) and Pd_2Ga, which must be the equilibrium phases. Fig. 8(a) shows a DF image from a spot indicated by a triangle in the corresponding (001) SAD pattern (Fig. 8(b)) of the specimen aged at 873 K for 1 ks, which corresponds to the hardness peak. Although weak spots were detected at each place indicated by arrows in Fig. 8(b), they could not be printed without disturbing the shape of the 220 spots. Thus, we show another print of such a 010 spot as an inset at the central reflection in Fig. 8(b). The diffraction pattern proves that three phases, α_1(fcc) + α_2(fcc) + Pd_2Ga
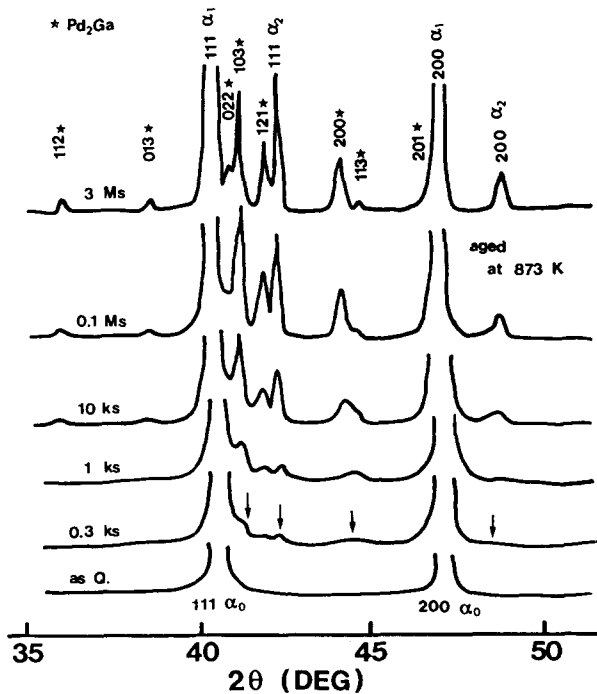
Fig. 7. Set of X-ray diffraction profiles of a Pd–Cu–Ga alloy annealed at 873 K for various times.

(orthorhombic) are produced similar to the XRD data (Fig. 7). The structure consists of very fine lamella of the Pd_2Ga and $(\alpha_1 + \alpha_2)$ as seen in Fig. 8(a). Considerable hardening should be expected in this specimen. As mentioned above, a spot indicated by an arrow in Fig. 8(b), must have been misinterpreted as that of an $L1_0$ phase by Odén and Herø [3].
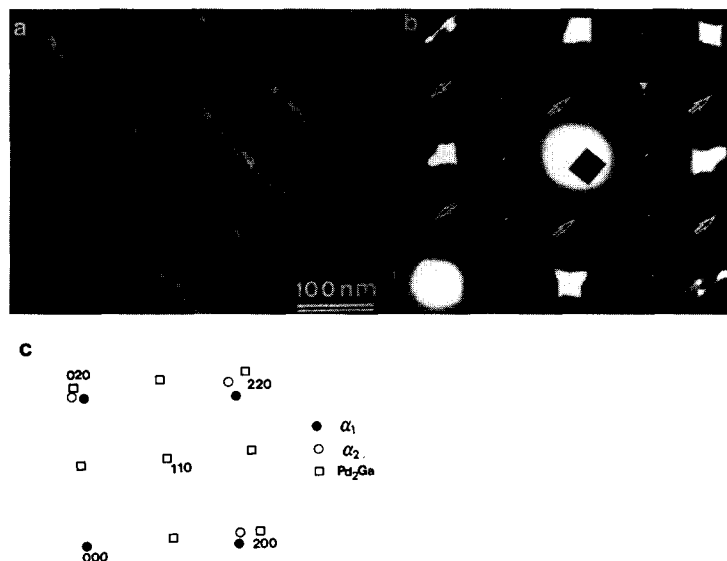
3.5. Two-way precipitations

Though the present alloy has the same stable phases $(\alpha_1 + \alpha_2 + Pd_2Ga)$ at 673 and 873 K, each precipitation behavior is different as mentioned above. At 873 K, stable phases are directly produced, while at 673 K a metastable phase with an $L1_0$ structure is produced on the way. It is of interest why such a difference occurred. We can speculate the reason by following an idea, in which Tong and Wayman [15] interpreted the appearance of a metastable phase in the Cu–Au alloy. The free energy vs. temperature for the α_0, β and $\alpha_1 + \alpha_2 + Pd_2Ga$ phases is schematically sketched in Fig. 9. T_1 is the transition temperature for $\alpha_0 \leftrightarrow \alpha_1 + \alpha_2 + Pd_2Ga$ and was about 920 K as seen in Fig. 1. If the alloy is originally at temperature T_0 and is slowly
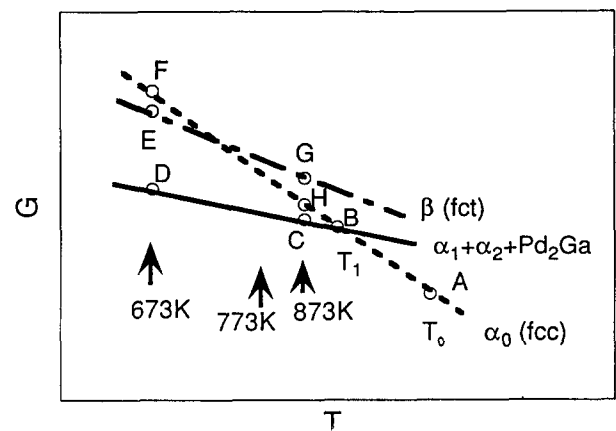

Fig. 9. Schematic diagram of free energy G with temperature T for the α_0, β and $\alpha_1 + \alpha_2 + Pd_2Ga$ phases.

Fig. 8. The 110 DF image of Pd_2Ga (a), the corresponding (001) SAD pattern (b), and its key diagram (c) of a Pd–Cu–Ga alloy annealed at 873 K for 1 ks. The key diagram proves the existence of three phases. Another print of a 010 spot is inset in the central reflection in (b), because some spots indicated by arrows in (b) were very faint.

cooled to maintain thermodynamic equilibrium, the change in free energy will follow a path ABCD. If the alloy is quenched from T_0 to 673 K and thus maintains the α_0, its free energy would correspond to point F. When the temperature is held at 673 K, the alloy will undergo a transition to the equilibrium phases (α_1 + α_2 + Pd_2Ga) in order to reduce its free energy. The free energy for the β phase falls between the two transition points F and D, and the formation of the β phase mixed with the matrix is expected, in agreement with the experimental results. The situation of 773 K annealing was similar to that of 873 K annealing, as expected from the hardness behavior in Fig. 4. On the other hand, the free energy of the β phase (point G) is higher than that of the α_0 phase (point H) at 873 K, and the α_0 may transform to the α_1 + α_2 + Pd_2Ga phase (point C) directly.

4. Conclusions

Phase transformation behavior in a dental Pd–Cu–Ga alloy was studied by means of hardness tests, electrical resistivity measurements, X-ray diffraction and transmission electron microscopy. The main results obtained are as follows.

(1) Annealing at 673 K produces two hardness peaks which correspond to the formation of a metastable phase with an ordered fct structure and the precipitation of the equilibrium phases, α_1(fcc) + α_2(fcc) + Pd_2Ga (orthorhombic), respectively.

(2) The annealing at 873 K exhibits only one peak due to the precipitation of the equilibrium phases.

(3) The difference of the phase transformation between both annealing at 673 K and 873 K having the same equilibrium phases was interpreted in terms of the free energy.

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