International Journal of Engineering & Technology, 8 (1.4) (2019) 183-190

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper



Effect of additional heat treatment of a Pd-Au-Ag metal-ceramic alloy on hardness change during simulated porcelain firing

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Abstract

This research aims to investigate the effect of softening for dental Pd-Au-Ag metal-ceramic alloy when further treated with second heat treatment through simulated porcelain firing. Through experimental procedures, it was found that the hardness rating of the alloy was very much consistent throughout, and after the degasification process. Results showed that further heat treatments on the alloy did not enhance its hardness rating. Hence confirming that hardness is not largely affected in initial stages of porcelain firing process. However, in the later stages, throughout the heating process, the hardness did not decline, but rather had a positive effect. The alloy consists of matrix lattices and precipitates. The matrices were in the form of a Pd-Au-Ag-rich (α) Å type face-centered cubic (FCC) structure with lattice parameter of a_{200}= 3.989, and the precipitates were Pd_3Sn (β) of $AuCu_3$ type.

Keywords: ***Keywords***: *Second Heat Treatment; Pd-Au-Ag Metal Ceramic Alloy; Simulated Porcelain Firing; Hardness change*

1. Introduction

Metal-ceramic prostheses for dental applications are generally manufactured through casting powdered dental porcelain in layers on a metal substructure then firing multiple times. The substructure must have a higher melting point that the porcelain and it must have high enough strength to withstand against the stress that occurs during fusion [1]. For metal-ceramic alloys, depending on the temperature during firing and the cooling rate after the firing, its mechanical properties can change. Yasuda et al mentions in a research relating to age hardening of dental alloys, that for alloys containing Pb, its hardness increases due to precipitation phase separation which causes lattice deformation [2, 4, 10, 16]. Furthermore, Hisatsune et al found that alloys consisting of 55 Pd-36 Ag-5 Sn-4 In (wt. %) decreases in hardness due to coarsening. Also depending on the composition, its hardness mechanism varied [2, 7]. If high temperatures were used in the furnace to fuse ceramic, it could degrade mechanical properties of the alloy which may lead to fracturing [7, 8, 10, 15].
Metal-ceramic prosthesis can be manufactured for natural teeth replacement and implant fixtures. The latter tends to have a shorter lifetime due to fatigue fracturing of the metal [12-13]. Skalak et al reported that on contrary to natural teeth prostheses, implant fixtures cannot dissipate biting pressures. It must have high hardness rating to function as a recovery bridge in preventing fatigue fracture [14]. Hence for final products, enhancing the mechanical property is of utmost importance for durability.

For the purposes of this study, Pd-Au-Ag alloy for metal-ceramic dental prosthesis substructure manufacture has been used. For creating implant supported bridge, alloy manufacturer recommends degassing prior to firing the porcelain then further heating for 15 minutes at 600˚C. According to this guideline a pilot study consisting of additional heat treatments were carried out. Results showed a definite increase for hardness when quenched after degassing, yet when the cooling rates were relatively slow, heat treatments showed no change for hardness property [9]. Following on from this finding, this study examines the Pd-Au-Ag alloy during the simulated porcelain firing procedure and analyzes its change, effect and mechanisms of hardening.

2. Materials and Methods

2.1. Specimen Alloys

Dental casting metal alloy of Pd-Au-Ag type for metal-ceramic dental prosthesis substructure manufacture has been used especially on dental implant for this study (Esteticor Implant®32, Cendres Metaux, Switzerland). The melting point and casting temperature given by the manufacturer ranges from 1215-1290˚C and 1390-1440˚C respectively. The compositions for the alloy was converted to atomic ratio

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(at.%) from weight ratio (wt.%) given by the manufacturer in Table 1. To cast the experimental specimen, phosphate bonded investment material (Univest plus, Metalor dental, Switzerland) was used for the die. The alloy was melted using oxygen-propane gas torch (for dental use) then cast via the use of a centrifugal casting machine (Kerrdental, Centrifigo, United states). The specimen was then annealed to room temperature and cleaned for 30 minutes in an ultrasonic cleaner (Easyclean, Renfert, Germany).



Fig.1: Casting with centrifugal casting machine

Table 1: Specimen Chemical Composition

Composition	Pd	Au	Ag	Sn	Ru	In
wt.%	40.85	32.00	19.00	5.00	0.15	3.00
at.%	48.45	20.51	22.23	5.32	0.19	3.30

2.2. Heat treatment

2.2.1. Degassing

The cast specimen was degassed in a dental porcelain furnace (Multimat, Dentsply, Germany) for 10 minutes at 900˚C without vacuum (from 600˚C to 900˚C at 55˚C climb per minute) afterwards, cooled to 600˚C. The cooling rate of the firing furnace after degassing stage was variously adjusted according to the closing speed of the firing chamber (Table 2).

2.2.2. Second heat treatment

The manufacturer recommends that the metal substructure for implant-supported bridge prosthesis be subjected to a special additional heat treatment (second heat treatment) to improve its fracture resistance. Therefore, the degassing treated specimens were subjected to second heat treatment at 600 ° C for 15 minutes in a porcelain furnace.

2.2.3. Simulated porcelain firing

The second heat treated specimen was then put under repetitive simulated firing processes until it following the manufacturers' instructions reached its final stage (Table 3).
rjui At the end of each firing cycle, the specimen was annealed at stage 2 rate then annealed to room temperature.



Fig. 2: Dental porcelain furnace

Table 2. Cooling stages of dental porcelain furnace

Cooling stage	0	1	2	3
*Condition	Firing chamber moves immediately to upper end position	Firing chamber opens about 70 mm	Firing chamber opens about 50 mm	Firing chamber remains closed - quick cooling

	- no controlled cooling			

* Using the 3 cooling stages of the porcelain furnace (Multimat 2 Touch) results in a stress relaxation in the ceramics. When cooling stages were programmed, the cooling starts after the end of the firing time, and lasts until the preheating temperature is reached again.

Table 3: Completion of Simulated Firing Cycle

Firing cycle	Pre-drying (min)	Pre-heating (℃)	Heating-rate (℃/min)	Vacuum level (hpa)	Final temp. (℃)	Hold time (min)
Degassing	0.25	600	55	50	900	15
2nd heat treatment	0	0	55	0	600	15
1st opaque	7	600	55	50	930	2
2nd opaque	7	600	55	50	930	2
Body	6	600	55	50	910	1
Glaze	3	600	55	0	890	1
Add-on	4	600	55	50	880	1

2.3. Hardness Test

After completion of heat treatments, the specimens were tested using Vickers hardness tester machine (MVK-H1, Akashi Co., Japan) under 300 gF for 10 seconds. Each specimen was tested 5 times and its value averaged to give final hardness rating.

2.4. Field-Emission Scanning Electron Microscope (FE-SEM)

FE-SEM (JSM-6700F, Jeol, Japan) was used to examine the structural changes in the simulated porcelain firing specimen. A micro grinder was then used to achieve a mirror-like finish on the test pieces and a solution consisting of 10% KCN (potassium cyanide) + 10% $(NH_4)_2S_2O_8$ (ammonium persulfate) was used to corrode the surface. Then the treated surface was exposed under the FE-SEM (JSM-6700F, Jeol, Japan) at an accelerated voltage level of 15kV.

2.5. X-ray Diffraction Analysis (XRD)

The polished specimen was tested by an X-ray diffractometer (XPERT-PRO, Philps, Netherlands) for X-ray diffraction with testing condition of 30kV, 40mA, scan rate 1˚ (2θ/min) and Ni filtered Cu K(α) radiation.

2.6. Energy Dispersive X-ray Spectrometer Analysis (EDS)

EDS (INCA x-sight, Oxford Instruments Ltd., UK) was used to investigate the proportion of elements in the specimen using accelerated voltage level of 15kV.

2.7. Statistical Analysis

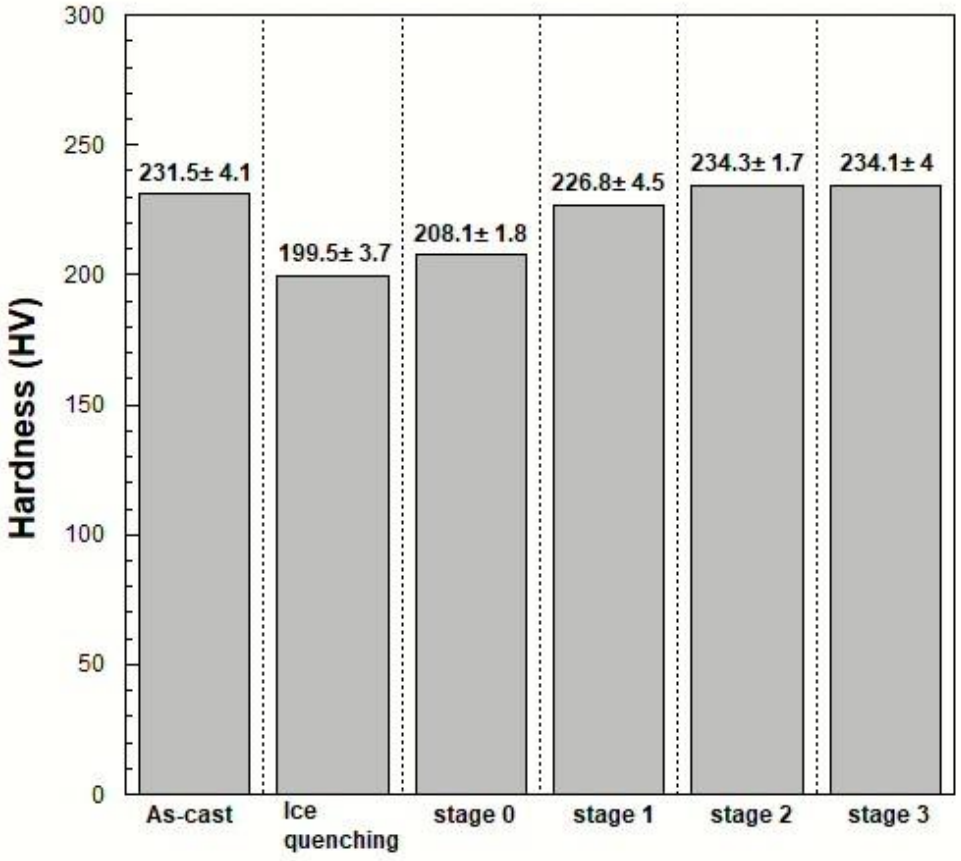
For statistical analysis, SPSS program (SPSS 23.0: SPSS IBM, Armonk, USA) was used. Hardness testing was analyzed using two-way ANOVA method (α=0.05), and through Post-Hoc, Tuckey HSD test was also carried out.

3. Results and Discussion

3.1. Hardness change with cooling rate

To determine how various cooling speeds had affected hardness of the experimental alloy, the specimens underwent simulated porcelain firing till degassing state. From then, hardness was measured upon being cooled at 4 different cooling rates (including ice quenching) outlined in Table 2. In figure 3, hardness values for annealed (as-cast; bench cooling) and ice-quenched samples have been recorded, compared and analyzed. The values were 231.5 HV and 199.5 HV respectively. As evident, for the latter specimen, hardness has dropped significantly indicating that it had softened during degassing phase.

The cooling rates impacted hardness of the alloy. Specimen cooled at stage 2 annealing rate had a hardness value of 234.3 HV which was comparable to the bench cooled specimen. From this, during degassing phase, the alloy softens, then as it cools, its hardness increases. Yasuda et al had reported that as dental metal-ceramic alloys cool upon solution heat treatments, due to precipitation and movement of lattices, hardness increases as a result [17]. In this study, at cooling rates lower than stage 2, hardness did not increase any further. Hence with time efficiency in mind, for metal-ceramic alloys of similar types, consistent use of stage 2 cooling rate would be believed to bring out the best of its hardenability. Hitsatsune et al had found through experimental methods, an average rate between slow annealing and quenching gave the best result for increasing hardness in alloys. Further reporting that it was due to change lattice structures in the process [6]. According to this finding, this experiment had been tuned to provide optimal environment for hardenability to manifest during cooling at stage 2



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Fig. 3: Hardness change of specimens by cooling stage after simulated porcelain firi

3.2. Effect of further heat treatment on hardness variation of the alloy

After degasification of cast specimens, and heat treating it for the second time according to manufacturers' recommendation, to investigate the effect porcelain furnace treatment has on them, both heat treated, and non-heat-treated specimens were treated through simulated porcelain firing until it reached the final (add-on) stage. According to the manufacturers' recommendation, specimens were further heat treated in porcelain furnace for 15 minutes from 600˚C then annealed using stage 2 rate (firing chamber open approx. 50 mm) after simulated porcelain firing at each stage. Out of the 4 cooling stages (including ice quenching) available for control with the porcelain furnace, stage 2 was the most effective for age-hardening the alloy [9]. Figure 4 shows the graph of change in hardness of the specimens with and without second heat treatment during the porcelain firing simulation. To see whether further heat treatments had any effect on the hardness, two-way ANOVA analysis was conducted, and its results showed in Tables 4-1 and 4-2. Table 4-1 shows variance in hardness depending on heat treatment ($p=0.001$) and
firing stage($p<0.001$), furthermore interaction between the two variables also showed to affect hardness ($p<0.001$). Observing in detail the interaction analyzed in Table 4-2, the specimens' hardness was approximately 234 HV, then it varied depending on the furnace stages during further heat treatments. Increase in hardness was not evident for degassed specimen for when it was in degassing stage and after it had been further heat treated. Passing through the 1st opaque stage, the two types of specimen both similarly decreased in hardness ($p<0.05$) and they showed similar values as well. Then not much change was evident through second opaque stage ($p<0.05$) until it reached the Body stage where hardness for the non-further heat-treated specimen fell ($p<0.05$). The trend continued until the final (add-on) stage, hence the difference in hardness between them increased.
Hardness of Pd-Au-Ag type metal-ceramic alloy is not largely affected by further heat treatment at the initial stages. However, in the latter stages of firing it was evident that it had positive impact on the hardness levels [8]. This implies that further heat treatment may act as a preventive measure for the alloys' decrease in hardness. Hence it seems likely that further heat treating the degassed alloy leads to strengthened durability for the finished prosthesis.

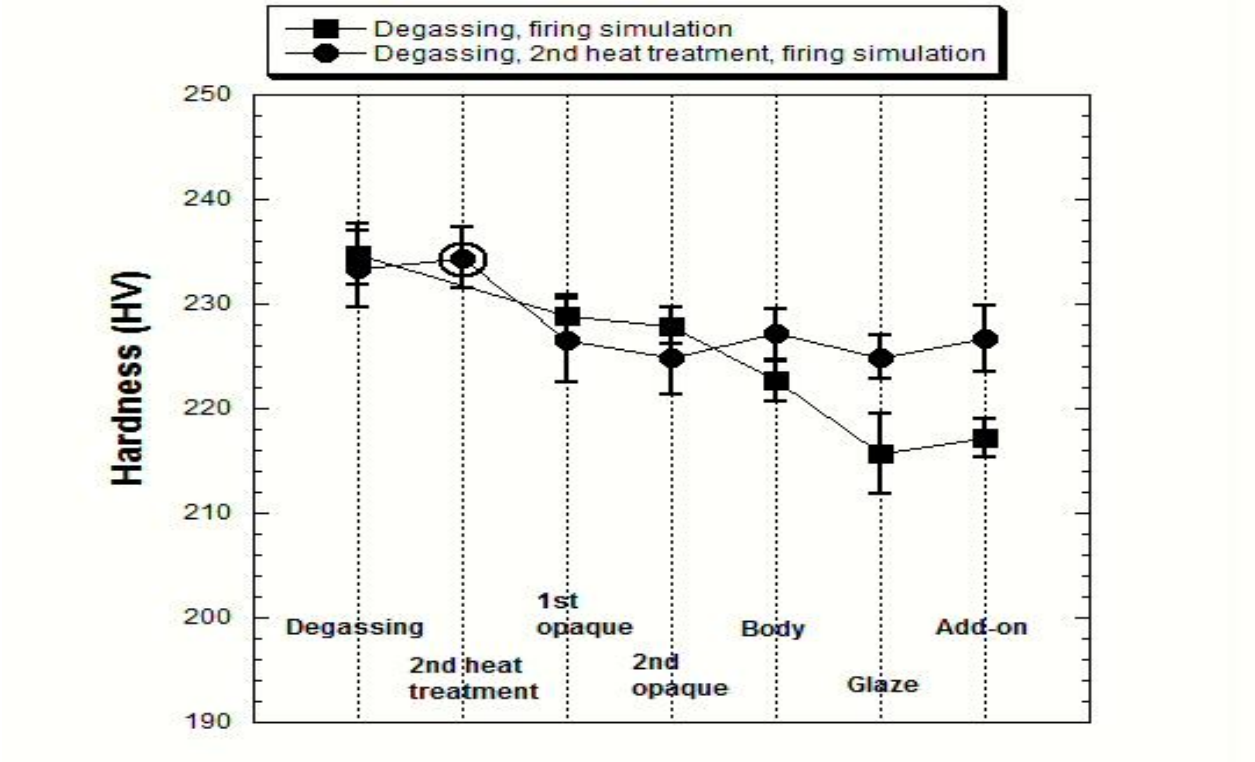


Fig. 4: Change in hardness of the heat treated/non-heat treated specimens during porcelain firing simulation.

Table 4-1: Statistics of hardness as a control of additional heat treatment and firing stage

Factor	F (p)
2nd heat treatment	13.584 (0.001)*
Firing step	28.688 (<0.001)*
2nd heat treatment × Firing step	10.136 (<0.01)*

*Statistically significant difference ($p<0.05$)
Statistical significance was analysed by a two-way ANOVA at a=0.05

Table 4-2: Statistics of hardness as a control of additional heat treatment and firing stage

2nd heat treatment	Hardness (HV)					
	Degassing (before 2nd heat treatment)	1st opaque	2nd opaque	Body	Glaze	Add on
Non-heat treated	234.70^{Ad} (±2.92)	228.82^{Ac} (±1.95)	227.88^{Ac} (±1.72)	222.62^{Ab} (±1.91)	215.68^{Aa} (±3.80)	217.18^{Aa} (±1.79)
Heat treated	233.40^{Ab} (±3.66)	226.46^{Aa} (±4.03)	224.76^{Aa} (±3.50)	227.10^{Ba} (±2.45)	224.92^{Ba} (±2.06)	226.62^{Ba} (±3.17)

The values are denoted as mean±standard deviation. Statistical significance was analyzed by a two-way ANOVA at a=0.05, followed by Tukey HSD test for multiple comparisons.
^{A,B} Statistically significant difference in the 2nd heat treatment.
^{a,b,c,d} Statistically significant difference for different firing stages.
Same uppercase letters indicate that there are no statistical differences between the 2nd heat treatment (Non-heat treated, Heat treated), and same lowercase letters indicate that there are no statistical differences among firing steps (Degassing-Add on).

3.3. Change in microstructure after simulated porcelain firing

FE-SEM was used to examine the effect on microstructure of the further heat-treated dental metal-ceramic alloy (degassed) during the simulated porcelain firing process. Figure 5 shows the microstructural changes during porcelain firing simulation for the 2 specimens at different magnification levels. In the degassed specimen (a), particle precipitates were observed in the grain interior. In the grain boundaries, particle and elongated precipitates were observed, and matrix was observed between the precipitates. In the specimens (b) subjected to additional heat treatment after degassing treatment, there was no significant change compared to the degassed specimen (a), but the amount of precipitate increased. And the spacing between the precipitates narrowed and the area of the matrix was reduced. At that time, the hardness value was maintained without significant change.
In Figure 6, homogenization has partially commenced for specimen (a) and (b), hence elongated precipitates have disappeared, and matrices have become evenly sized and structured. Hardness of both specimens were lower than when they were only degassed ($P<0.05$). For specimen (b) the amount of matrices was relatively small due to narrow spaces between precipitation grains. Coarsening of precipitates within and at grain boundaries were observed for specimen (c) ($P<0.05$) which seemed to have led to a reduction in hardness [3,

10]. For specimen (d), although coarsening of the precipitates is visible, as it only occurred within grain boundaries, hardness was not decreased ($P<0.05$). Results from this observation show, that for the final hardness comparison in Table 4-2, the heat-treated specimen showed higher hardness values as further heat treatment had prevented coarsening of precipitates within and at grain boundaries.

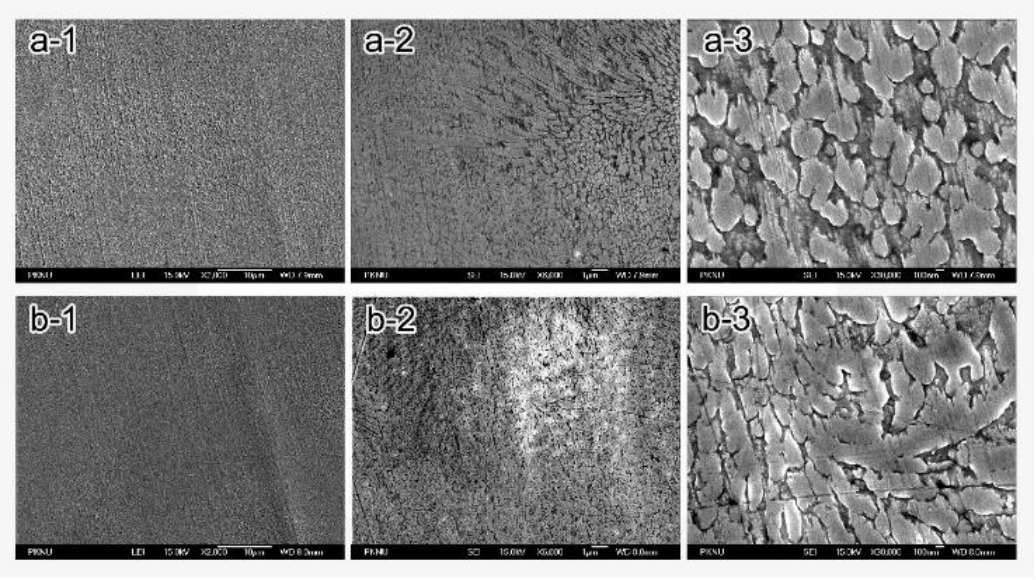


Fig. 5: Microstructural changes during simulated porcelain firing:
(a) degassed, non-heat treated specimen
(b) degassed, heat treated specimen
At magnifications of x2000 (1), x6000(2), x30000(3)

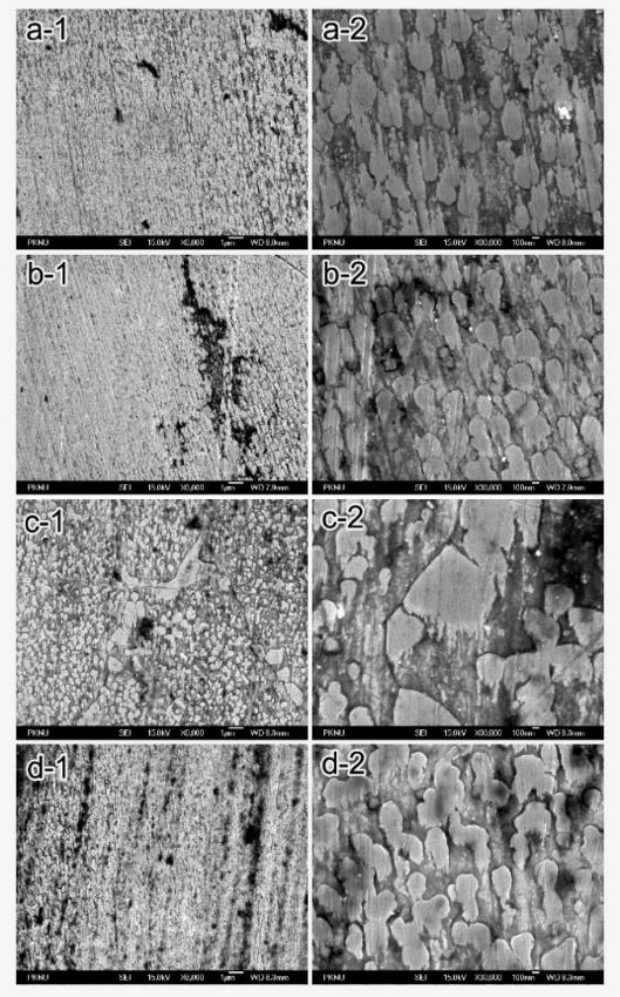


Fig. 6: Microstructural changes during simulated porcelain firing:
(a) 1st opaque stage, non-heat treated
(b) 1st opaque stage, heat treated
(c) add-on stage, non-heat treated
(d) add-on stage, heat treated
At magnifications of x6000 (1), x30000(2)

3.4. Change in phase transformation during simulated porcelain firing

XRD was used to examine the changes in microstructure of the specimens and the results are shown in Figure 7.
The Pd-Au-Ag type alloy used for this study consisted of single phase matrices (α) Å type face-centered cubic (FCC) structure with lattice parameters of a_{200}= 3.989. However, as shown in the microstructure observation of this experiment, it was confirmed that the crystal structure was divided into matrix and various types of precipitates during simulated firing process and composed of at least two kinds of phases (Fig. 5, 6). Kim et al reported that when the precipitated two phases have similar lattice parameters, the overlap of phases occurs, and that XRD analysis results in overlapped one peak. [9]. Therefore, in the XRD results in this study, it was thought that the diffraction peaks of single phase appeared because the two phases, which have very similar lattice parameter, overlapped and appeared to be single phase. For verification, EDS analysis was carried out. Figure 5 and Table 4 shows the FE-SEM image and EDS analysis result for specimen without additional heat treatment after it has been through simulated porcelain firing. Compared to the alloy composition in Table 1, matrices have slightly decreased in Pd, Sn and In content whereas Au and Ag has slightly increased.
For precipitates it was vice versa, Pd and Sn massively saw an increase and Au and Ag greatly decreased. The effects were more evident for P2 and P3 cases and "In" content was clustered at grain boundaries rather than within. The size of the EDS probe could have possibly influenced this outcome as it was in fact larger than the precipitate size within the grains. Furthermore, the results provide evidence that the matrices are Pd-Au-Ag rich (α) types with Å type face-centered cubic (FCC) structure with lattice parameters of a_{200}= 3.989. Then considering the Pd and Sn content levels, precipitates must be $AuCu_3$ type of Pd_3Sn (β). According to references, lattice parameters for these precipitates are generally a= 3.971 [16].
Guo et al reported that depending on the solubility property of the metal-ceramic alloy, after homogenization at elevated temperatures, during cooling phase separation will occur and lattice parameters become different with movement, this is reported to be the mechanism behind enhancement of hardness in the alloy [5, 11, 17].
For this study, for the secondary heat-treated specimen, as the lattice sizes between matrices (α) and precipitates (β) were of similar dimensions, lattice movement which causes hardness increase was not present. Hence hardness was purely maintained and did not rise.

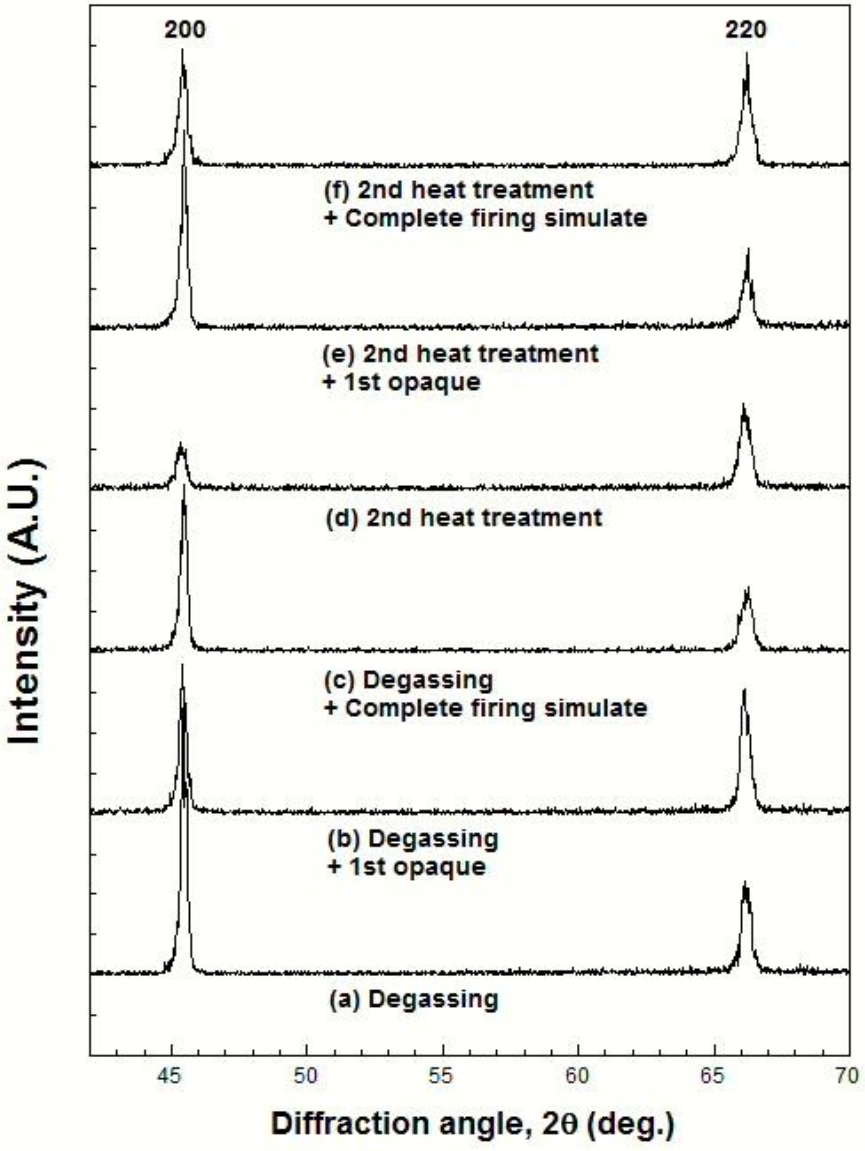


Fig. 7: Change in the XRD pattern during simulated porcelain firing

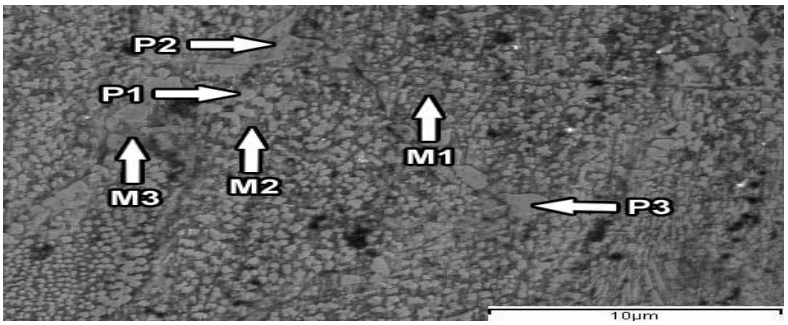


Fig. 8: FE-SEM image of non-heat treated final stage (add-on) specimen (M: Matrix, P: Precipitates)

Table 5: EDS analysis at the regions marked in Fig. 8

at.%		Pd	Au	Ag	Sn	Ru	In
Matrix	M1	45.16	25.59	26.31	2.95	0	0
	M2	46.20	25.75	24.08	3.97	0	0
	M3	45.16	25.29	26.31	2.95	0	0
Precipitate	P1	63.82	13.73	10.30	12.15	0	0
	P2	74.06	5.36	0	16.99	0	3.59
	P3	75.01	4.62	0	17.19	0	3.19

4. Conclusion

In conclusion upon observing the effects of secondary heat treatment on softening of Pd-Au-Ag type metal-ceramic alloy, following results have been obtained.

1. As hardness was found to be nearly identical before and after the degassed specimen underwent secondary heating, further heat treatment alone does not increase hardness of the alloy.
2. At initial stages of simulated porcelain firing, additional heat treatment of the alloy did not largely affect its change in hardness.
3. At latter stages of simulated porcelain firing, additional heat treatment of the alloy had a positive effect on the alloy by maintaining its hardness level.
4. The alloy consisted of matrices of Pd-Au-Ag rich (α) Å type face-centered cubic (FCC) structure with lattice parameters of a_{200}= 3.989 and the precipitates were Pd_3Sn (β) of $AuCu_3$ type.

Acknowledgement

This study and thesis had the support of and was funded by Gimcheon University (No: GC16096).

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