

CHARACTERISATION OF PHOSPHATE-BONDED INVESTMENTS FOR PLATINUM CASTING

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Abstract

Platinum jewelry is manufactured by investment casting process. Phosphate-bonded investment is used to make a mold for platinum to withstand a high melting temperature above 1,700°C. The investment powder composes of quartz to provide thermal expansion to compensate the subsequent contraction of the alloy. Two types of commercial phosphate-bonded investment materials for platinum casting with different particle size distribution were investigated. The microstructural analysis and thermal behavior, chemical composition and crystal structure of the investments were analyzed. The investment composed mainly of SiO₂ as refractory material with aluminium phosphate-based binder. During the burnout step, silica experienced α -quartz inversion resulting in change of the interplanar spacing and crystallite size for the investment after firing. The fineness of the investment powder related directly to surface quality of the as-cast platinum jewelry in term of surface smoothness and casting defects.

Keywords: Platinum casting, phosphate-bonded investment, lost-wax casting, investment casting, jewelry

Introduction

Investment casting also known as lost wax casting is a general manufacturing process for jewelry metals and alloys including platinum group. As illustrated in Figure 1, the investment casting process composes of wax-mold making, wax-tree forming, investment mixing and setting, wax burning-out and investment- mold baking, and finally metal casting (Niyomsoan *et al.*, 2017). Quality of the as-cast metal jewelry depends on many process parameters including properties of the investment (Lester *et al.*, 2002; Carter, 2004; Klotz and Drago, 2011). Phosphate-bonded investment has been used for platinum jewelry with a high casting

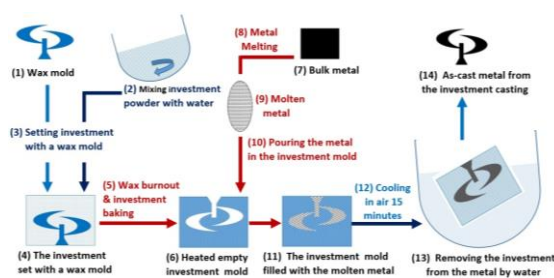


Figure 1. Scheme of an investment casting for jewelry manufacturing

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range between 1,710°C-1,790°C (Heiss *et al.*, 2015; Maerz, 2020). The investment composes mainly of refractory powder and binder to withstand the molten metal at high temperature. The refractory powder is generally silicon dioxide (SiO_2) partly or mostly in form of quartz to provide thermal expansion in compensation with casting shrinkage of the metal (Alsa'ady, 2008; Abdul-Razzak *et al.*, 2014). The binder plays an important role for shaping the investment mold through the casting process (Horton, 2004). There are many types of binder for commercial phosphate-bonded investment materials such as magnesium ammonium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (Abdul-Razzak *et al.*, 2014), magnesia/alumina/silica based (Khurana *et al.*, 2020), and monoaluminum phosphate ($\text{Al}(\text{H}_2\text{PO}_4)_3$) as a heat-resistant binder (Liu *et al.*, 2011; Taki Chemical, 2019).

The present research was to investigate a behavior of the commercial phosphate-bonded investments for platinum casting, with the influence on the as- cast metal jewelry. The study focused on the investigation of particle sizes of the investment powders, microstructural features, crystal structures and phase transformation during heating in the investment casting process. Moreover, the resulted as- cast platinum jewelry using different types of investments were also investigated.

Materials and Methods

Two commercial phosphate-bonded investment powders for platinum casting were investigated entitled "Investment A" and "Investment B". The investment slurry was prepared by mixing the powder with de-ionized water that was pre-mixed with binder. The mixed investments were set at room temperature for 4 h. The hardened slurry was so called 'green sample'. It was processed through the wax burnout and investment baking process for platinum casting following the temperature profile in Figure 2. Subsequently, three Pt-0.35wt.% Co jewelry pieces were cast for each type of investments. Surface quality of the as-cast samples was investigated under optical stereo microscope by the quality control department regarding a commercial quality level.

Particle size of investment powder was analysed using the Malvern Panalytical Mastersizer 2000 laser diffraction testing instrument. Chemical analysis of the powder samples was performed using Bruker S8Tiger X-ray fluorescence spectrometer (XRF), respectively. Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the green sample were carried out in Netzsch STA 449 F3 Jupiter thermal analyzer. The measurement

was performed under a constant argon flow rate from room temperature up to 950°C, with heating rate of 10°C/min. FEI Quanta 450 Field Emission Scanning Electron Microscope, (FESEM) equipped with Oxford Instrument ED 2000 energy-dispersive spectroscopy (EDS) was used for microstructural analysis of the investments in form of as-received powder, green sample and fired sample. The crystal structure was investigated using Rigaku Smartlab X-ray Diffractometer (XRD) with Cu K_α radiation (1.5406 Å) at step size of 0.02 deg and scanning speed of 5.34 deg/min.

Results and Discussion

Particle Size Distribution and Chemical Analysis

The particle sizes of the as-received investment powder were evaluated using the laser diffraction particle size analyzer. Figure 3 shows the particle size analysis with (a) the particle size distribution curve in volume percentage including (b) the

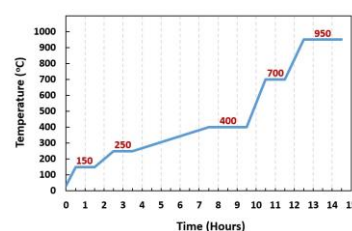


Figure 2. Temperature profile for wax burnout and investment baking

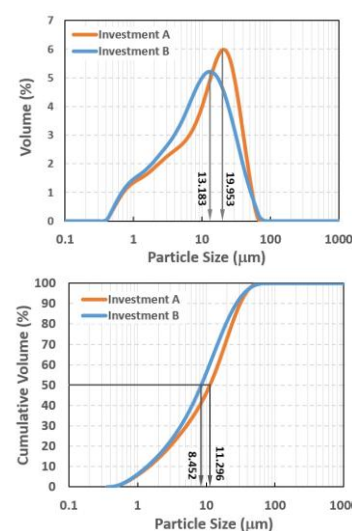


Figure 3. Particle size profiles of the investment powders represented in (a) particle size distribution curve, and (b) particle size accumulation curve

Table 1. Particle sizes of investment powder

Investment sample	Particle size (μm)					< 1 μm (Vol.%)	> 60 μm (Vol.%)	Span*
	D ₁₀	D ₂₅	D ₅₀	D ₇₅	D ₉₀			
Invest. A	1.370	3.952	11.296	21.116	27.342	15.962	0.846	2.30
Invest. B	1.468	3.400	8.452	16.659	31.198	17.227	1.298	3.52

*Particle distribution width calculated according to Eq.(1)

Table 2. Chemical analysis of the investments

Investment Type	Chemical compositions (wt%)									
	SiO ₂	P ₂ O ₅	Al ₂ O ₃	CaO	Fe ₂ O ₃	TiO ₂	K ₂ O	Cl	SrO	Trace < 0.01
Invest. A	98.9	0.54	0.31	0.12	0.03	0.02	0.02	0.02	-	ZrO ₂
Invest. B	98.7	0.62	0.43	0.13	0.03	0.02	0.05	-	0.01	CuO, NiO

accumulative curve. The accumulative data of the particle sizes are shown in Table 1. Their sizes range from less than 1 μm to at least 60 μm , the maximum particle sizes are 60.256 μm and 69.183 μm for Investment A and Investment B, respectively. Particle sizes with the highest volume percentage were 19.95 μm and 13.18 μm for Investment A and Investment B, respectively. Shape of the curves represented the broad size distribution with continuity. The average particle size distribution of Investment A (D₅₀ of 11.296 μm) was slightly coarser than that of Investment B (D₅₀ of 8.452 mm). However, width of the size distribution of Investment A (span = 2.30) was narrower than that of Investment B (span = 3.52) as calculated for the value of span of the cumulative curve according to Equation (1) (Horiba Instrument, 2021):

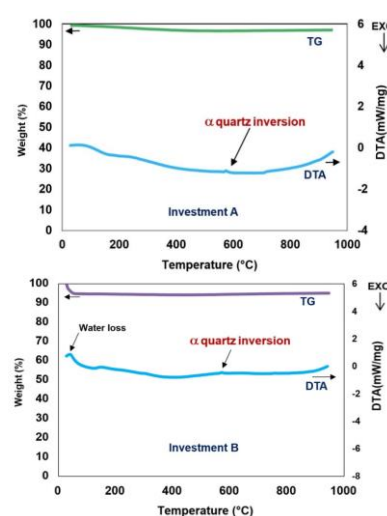
$$\text{Span} = (D_{90} - D_{10}) / D_{50} \quad (1)$$

where D₁₀, D₅₀, D₉₀ referred to the cumulative 10%, 50%, 90% particle sizes, respectively.

Table 2 shows chemical analysis of the as-received investment powder. The investments mainly contained silica (SiO₂) for more than 98 wt% as refractory powder. P₂O₅ and Al₂O₃ were found in both types of the powders indicating that the binder was aluminum phosphate-based as a heat-resistant binder (Taki Chemical, 2019). Other compounds were included as modifiers to provide an effective performance of the investment and a non-oxidizing atmosphere in the mold during casting.

Thermal Behavior and XRD Analysis

The green sample was heated to 950°C to investigate the thermal behavior in the working situation of the investment casting process for platinum jewelry. DTA analysis showed an endothermic reaction at 567-573°C in Figure 4 which corresponded with ' α -quartz inversion' (Johnson *et al.*, 2021). SiO₂ experienced phase transformation from trigonal α quartz, stable at low temperature, into hexagonal

**Figure 4 DTA/TG analysis of the green samples**

β -quartz, higher-symmetry phase and stable at high temperature. Such transformation was accompanied by a linear thermal expansion which was theoretically 0.45% (Akhaven, 2014; Sai-intawong, 2008; Lohwongwatana *et al.*, 2017). In addition, for Investment B, an endothermic reaction at 76.5°C indicated a release of water molecule corresponding with weight loss by TG analysis in Figure 4(b). As Investment B hold more water molecule in the green sample resulting in shrinkage due to the water loss reaction. However, such shrinkage would be compensated by the thermal expansion according to the quartz inversion. Such inversion was also observed in gypsum-boned investment during heating in the burnout process (Ingo *et al.*, 2005; Lohwongwatana *et al.*, 2017).

XRD analysis reveals the crystallinity of the investment in Figure 5. The XRD patterns of α quartz and aluminium phosphate were observed in the as-received powder and the samples after firing. Heiss *et al.* (2015) also reported that the α quartz from the investment was found to be intact

with surface of the as-cast platinum jewelry. The characteristic peak of quartz with the highest intensities was located (101) peak. Data of XRD analysis of the (101) peak are given in Table 3. The diffraction peak shifted to lower Bragg angles for the fired sample, as clearly seen in the insets for (101) main diffraction peak of α quartz. The shift corresponded with an increase of the interplanar spacing after firing as a result of thermal expansion as seen in Figure 6(a). Moreover, X-ray line broadening was identified with FWHM of the (101) peak, which reflected the fine crystallite size calculated using Scherrer equation in Equation (2);

$$D = 0.9\lambda / B \cos\theta \quad (2)$$

where λ is wavelength of X rays, B is half width at full maximum and θ is the diffraction angle. Figure 6(c) shows that the average crystallite size of the investment became smaller after firing due to

the α -quartz inversion reported by DTA. The anisotropic changes in cell volume accompanied with the α - β phase transition in quartz during the up-and down-temperature facilitated recrystallization and brittle damage (Johnson *et al.*, 2021).

Microstructural Analysis

SEM images of the investment powder in Figure 7 shows powder particles in irregular shape with a variation in sizes as reported by particle size analysis. Figure 8 shows SEM images of the green samples, which were agglomerates of SiO_2 particles at mainly smaller size than that of the powder. EDS analysis also showed the distribution of aluminum phosphate-based binder. Figure 9 shows morphological features of the fired investment resulted from the wax burnout and investment baking process up to 950°C (Figure 2) and then cooling down. The particles experienced the α - β quartz inversion with an expansion during the up-temperature transition and

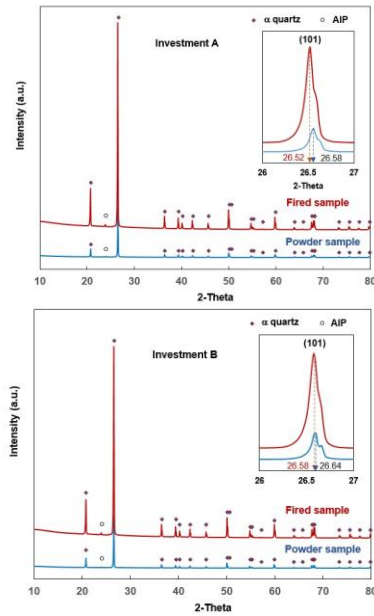


Figure 5. XRD patterns of the investments for powder and fired samples including the insets of (101) peaks. AIP indicates aluminium phosphate phase

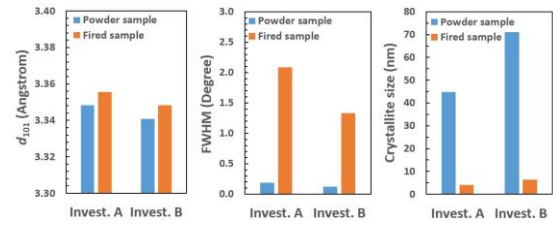


Figure 6. XRD (101) peak analysis for the investments as powder and fire samples; (a) d-spacing of (101), (b) FWHM of the (101) peak and (c) the corresponding crystallite size from Scherrer Equation

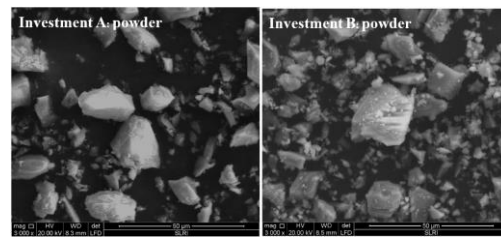


Figure 7. SEM images of the investment powders

Table 3. XRD analysis of the (101) peak showing peak shift and widening

Investment sample	(101) position (2 Theta)	d_{101} (Angstrom)	FWHM (Degree)	Crystallite size* (nm)
Invest. A				
Powder sample	26.58	3.35	0.19	44.8
Fired sample	26.52	3.36	2.09	4.1
Invest. B				
Powder sample	26.64	3.34	0.12	71.0
Fired sample	26.58	3.35	1.33	6.4

*Calculated by Scherrer Equation according to Equation (2)

a contraction during the down-temperature transition promoting microcracks to the fired sample (Johnson *et al.*, 2021). The EDS analysis revealed mostly the silica particles with a few alumina but phosphate remained from the binder.

Optical Microscopic Observation

The platinum rings were cast with Investment A and Investment B following the investment casting process shown in Figure 2. The as-cast surface quality of the rings was investigated using optical stereo microscope as shown in Figure 10.

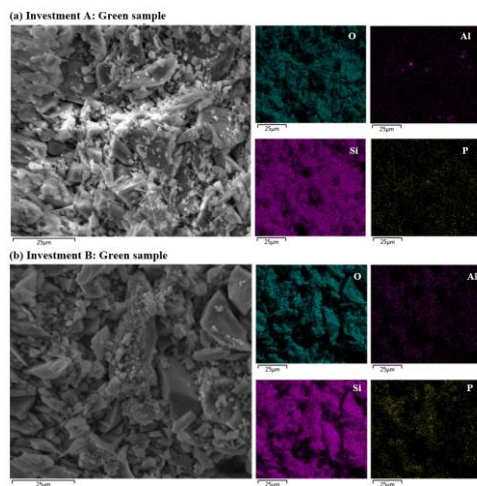


Figure 8. SEM images and EDS analysis of the green samples

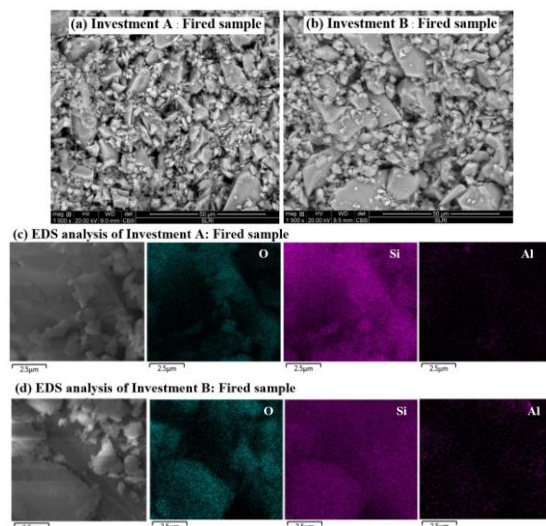


Figure 9. SEM image and EDS analysis of the fired samples; (a-b) SEM image of fired samples of Investment A and Investment B, and (c-d) EDS analysis of fired samples of Investment A and Investment B

The observation showed that surface of the platinum rings cast with Investment B were smoother than that with Investment A. Investment B composed of the powder particles with smaller average size ($D_{50} = 8.452 \mu\text{m}$, span = 3.52) but wider span of the size variation than that of Investment A ($D_{50} = 11.296 \mu\text{m}$, span = 2.30). The finer particles with wider span create finer voids among particles, which resulted in a smoother surface of the investment mold in contact with the molten metal. Consequently, the as-cast the platinum ring cast from the finer investment B created smoother surface than that from the coarser Investment A. The result was consistent with Yaman and Cigdem (2010) which reported effects of the particle size of investment powder on the quality of the investment casting.

From an investigation of the quality control staff as shown in Figure 10, approximately 15 points of surface defects were found on the rings cast from Investment A. For the rings cast from Investment B, there were averagely 27 points of surface defects, which were also gas porosity. All surface defects were mainly gas porosity.

Study of Yaman and Cigdem (2010) showed that the investment powder with finer particle size creating finer pore in the investment mold after setting. However, these finer pores lower gas permeability from the melt, which means difficult

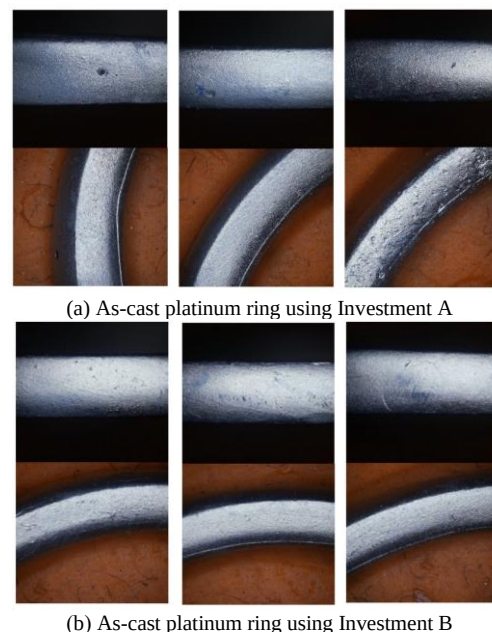


Figure 10. Optical stereo microscopic images of the as-cast platinum rings from investment casting using (a) Investment A and (b) Investment B (5X for bottom images and 10X for top images)

gas evacuation. The remain gas in the melt eventually forms gas porosity in the cast.

Accordingly, in the present study, higher amounts gas porosity was found in the smoother platinum ring cast with Investment B in comparison with Investment A with larger pore size and higher gas permeability.

Conclusions

The phosphate-bond investment for platinum casting consisted mainly of α quartz silica with a few percentages of aluminium phosphate. Quality of the as-cast platinum rings depended mainly on the particle size and size distribution of the powder. The platinum surface is smoother when casting using investment with smaller particles size and wider size span. However, more gas porosity in the cast was generated due to a more difficulty of gas evacuation. In the jewelry industry, smoothness of the surface is more desirable for aesthetic propose.

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References

- Abdul-Razzak, N.H., Al-Nuzal, S.M.D., Mustafa, M.A., Ali, F.H., and Lafta, B.A. (2014). Preparation of dental phosphate-bonded investment to cast nickel-chromium alloys and the evaluation of its mechanical and physical properties. *World J. Pharmaceut. Res.*, 3(9):173-179.
- Akhaven, A.C. (2014). The silica group. The quartz page. Available from: <http://www.quartzpage.de/>. Last modified date: Jan 12, 2014.
- Alsa'ady, A.A. and Gholam, M.K. (2008). The effect of additives on the linear thermal expansion of Phosphate-bonded investment. *Mustansiria Detal J.*, 5(1):7-13.
- Carter, R. (2004). Does investment permeability impact jewelry castings?, The SantaFe Symposium; May 2004. Albuquerque, USA, p. 105-119.
- Heiss, T., Klotz, U.E., and Tiberto, D. (2015). Platinum investment casting, part I: simulation and experimental study of the casting process. *Johnson Matthey Technol. Rev.*, 59(2): 95-108
- Horiba Instruments Ltd. (2021). A guide book to particle size analysis. Available from: https://ats-scientific.com/uploads/PSA_Guidebook.pdf. Accessed date: April 4, 2021.
- Horton, R. (2004). High temperature investment material and method for making solid investment molds. US Patent: US20040221768A1
- Ingo, G.M., Riccucci, C., de Caro, T. (2005). Thermal stability and chemical physical features of gypsum-bonded investment with regard to burnout cycle. The SantaFe Symposium May 2005. Albuquerque, USA, p.255-273.
- Johnson, S.E., Song, W.J., Cook, A.C., Vel, S.S., and Gerbi, C.C. (2021). The quartz $\alpha \leftrightarrow \beta$ phase transition: Does it drive damage and reaction in continental crust?. *Earth Planet. Sci. Lett.*, 553:116622
- Khurana, P., Singhal, R., Agarwal, S.K., Maheshwarl, R., Javed, B., and Kalpana, K. (2020). Investment materials: a review. *European J. Pharmac. Med. Res.*, 7(7):457-461.
- Klotz, U. and Drago, T. (2011). The role of process parameters in platinum casting. *Platinum Metals Rev.*, 55(1):20-27. Doi: 10.1595/147106711X540373.
- Lohwongwatana, B., Puncreobutr, C., Phetrattananangsi, T., Khamkongkaeo, A., Thongchai, C., Nisaratanaporn, E., Sakkomolsri, B., and Kuimalee, S. (2017). X-ray diffraction analysis, calorimetric and thermogravimetric characterization and topographic study of gypsum-bonded investment materials. The SantaFe Symposium; May 2017, Albuquerque, USA, p. 1-18.
- Liu, Q., Cheung, N. C. O., Garcia-Bennett, A. E., and Hedin, N. (2011). Aluminophosphates for CO₂ separation. *Chem. Sus. Chem.*, 4(1):91-97. DOI:10.1002/cssc.201000256
- Maerz, J.J. (2020). Platinum alloy applications for jewelry. Ganoksin jewelry making resources. International Gem Society LLC. Available from: www.ganoksin.com/article/. Accessed date: Jan 29, 2020.
- Niyomsoan, S., Vongchaisri, K., and Chanmuang, C. (2017). Study of Cu-based shape memory alloys from an investment casting process. The 7th National and International Graduated Study Conference (NGSC & IGSC 2017) and the 2nd National and International Conference on Creative Multi-disciplinary Studies for Sustainable Development (NCMSD & ICMSD 2017); July 20-21, 2017; Bangkok, Thailand, p. 20-27.
- Lester, P., Taylor, S., and Süß, R. (2002). The effect of different investment powders and flask temperatures on the casting of pt alloys. The SantaFe Symposium; May 2002; Albuquerque, USA, p. 321-334.
- Sai-intawong, K. (2008). Fracture defects in ceramic products. Thai Ceramic Society. com. Available from www.thaiceramicsociety.com. Accessed date: Jan 30, 2020.
- Taki Chemical. (2019). Aluminum Phosphate-based binders. Taki Chemical Co. Ltd. Available from www.takichem.co.jp/eng/products/ Accessed date: April 17, 2019.
- Yaman, B. and Cigdem, M. (2010). Effect of particle size variations of gypsum bonded investment powders on metallurgical quality of investment castings. *Int. J. Cast Metals Res.*, 23(1):60-64.