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Nano-engineering of zirconia–noble metals composites

Oleg Vasylkiv[a,b,*], Yoshio Sakka[a], Yasuaki Maeda[c], Valeriy V. Skorokhod[b]

[a]*National Institute for Materials Science, 1-2-1, Sengen, Tsukuba, Ibaraki, 305-0047, Japan*
[b]*Institute for Materials Science, NASU, 3, Krzhizhanivs'kogo Str., Kiev, 03680, Ukraine*
[c]*College of Engineering, Osaka Prefectural University, 1-1, Gakuencho, Sakai, Osaka, 599-8531, Japan*

Abstract

The possibility of preparation of Pt–3Y-TZP and Pd–3Y-TZP nano-composites was studied. The sonochemically synthesized Pt (Pd) nano-particles (~2 nm) were impregnated into zirconia nano-aggregates (20–45 nm). The morphology manipulation technique allowed production of the composite zirconia-based aggregates in which a significant fraction of the Pt (Pd) crystallites was embedded into the zirconia dense aggregates. Using the colloidal technique and low-temperature (1150 °C) sintering, we prepared the Pt (Pd)–zirconia (0.5–1.5 wt.% of platinum) nano-composites with average 3Y-TZP grain sizes of 120 nm, and with the Pt (Pd) grain size in the range of 20–60 nm.

Keywords: Nanocomposites; Powders-chemical preparation; Suspensions; ZrO_2; Metallic inclusions

1. Introduction

The addition of a metal to the ceramic matrix often produces a composite with more desirable properties than the individual components.[1,2,7–10] Nanometer-scaled clusters are very interesting in that their properties are between those of the condensed matter and atoms.[1,3–8] These clusters also provide excellent models for the study and understanding of surfaces and catalysis.[1,7,8]

The specific advantages of nanocrystalline materials are superior phase homogeneity and possible low-temperature sinterability.[1,3–6] Nanopowder production techniques are needed for engineering high-quality powders with required composition, homogeneity and morphology. These characteristics significantly determine the later-stage processing and final properties of the ceramic (or metal/ceramic composite).[1–9,13–15]

The chemical effects induced by ultrasound (20 kHz to 10 MHz) do not come from the direct interaction of sound with the molecule species. In the liquid phase, the wavelength of the sonic wave is in the range of a centimeter to micrometers, which is not a molecular dimension. The origin of the sonochemical reactions is the cavitation.[11,12] More specifically, cavitation occurs due to the stress induced by passing of the sound waves through the liquid. The sound waves consist of compression and decompression cycles. The pressure during the decompression is low enough for the liquid to be torn apart and leave bubbles. Such cavitation bubbles are the main driving force of the sonochemical processing.[11–14] The bubbles grow during the decompression cycles, and subsequently implode during the compression cycles. The bubbles are filled with vapor gases, and produce radicals during the implosion. Every one of the imploding bubbles is a kind of microreactor with a very high temperature and a pressure of the several hundreds of atmospheres inside. The concentration of energy during the multi-bubble collapse is enormous and the interior bubble temperature reaches thousands of degree during collapse.[11] The reaction rates are usually enhanced because of the formation of highly reactive radical species thus their reduction is facilitated.[12–14] In the sonicated system, three kinds of reducing species may be generated from the direct sonolyses of solvent water of solute sodium dodecyl sulfate (SDS) in the interfacial region of collapsed bubbles/neighboring volumes of liquid, and (or) the subsequent reaction between these radicals and SDS.[13,14]

The possibility of engineering of Pt and Pd–3Y-TZP composite nano-aggregates was studied in this

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* Corresponding author.
E-mail address: oleg.vasykiv@nims.go.jp (O. Vasylkiv).

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investigation. We reported that Pt(II) and Pd(II) ions were sonochemically reduced from aqueous solutions of their salts onto the surface of the aggregated zirconia crystallites to form platinum and palladium nanoparticles impregnated into the zirconia (3Y-TZP) nano-aggregates.

2. Experimental procedure

The preparation conditions of the 3Y-TZP nanopowder have been described in previous publication.[3] Reagent-grade potassium tetrachloropaladate (K_2PdCl_4) (produced by Kanto Chemical Co., Tokyo, Japan), potashium tetrachloroplatinate (K_2PtCl_4) and sodium SDS (both produced by Wako Pure Chemicals Co., Osaka, Japan) as a surfactant were used in this study. K_2PtCl_4 and K_2PdCl_4 stock aqueous solutions with SDS were initially prepared and aged for 12 h at 20 °C. The concentration of surfactant (SDS) of 8 M per 1 M of K_2PtCl_4 was applied.[13,14]

Two synthesis routes were used to determine the effect of the synthesis methods on the resulting properties of the Pt (Pd)–3Y-TZP composites. In both synthesis routes, the initial amount of Pt (Pd) compounds varied according to the final concentration of metal in the metal–ceramic composites between 0.5 and 5 wt.%. In both cases, the aqueous suspension of zirconia powder was impregnated with an aqueous solution of K_2PtCl_4 or K_2PdCl_4.

The following sonochemical reduction of Pt(II) ions to metal platinum (route A) was applied. A multiwave ultrasound generator (model Kaijo 4021, Tokyo, Japan) with a 65 mm diameter barium titanate oscillator was used for the ultrasonication. The generator operated at 200 kHz with an input power of 200 W. One hundred millilitres of every sample solution was placed in a cylindrical glass vessel with a 50 mm inside diameter and total volume of 150 ml, than purged with an argon gas stream. The vessel was mounted at a constant position relative to the nodal plane of the sound wave (3.75 mm, i.e. the half length of the ultrasound wave from the oscillator). The vessel was fixed at exactly the same position and closed during the irradiation. To maintain the constant temperature of 20 °C, the ultrasonic treatment was carried out in a temperature controlled water bath.

After the ultrasonic treatment, the suspensions were mixed using a magnetic stirrer with heating (150 °C) for a prescribed time (route B). Subsequently, the powders were separated from the supernatant by centrifuging (10 000 rpm for 15–20 min). The composite powders were then washed several times with distilled and deionized water to remove the chloride ions and the products of the SDS decomposition. Washing with water was followed by ethanol (C_2H_5OH, 99.5% reagent grade, Kanto Chemicals, Japan) washing with subsequent centrifuging, redispersing in fresh ethanol and then a final slow evaporation of the ethanol ($T = 60$ °C) using a drying oven. After each wash cycle, the washed composite powders were redispersed in water or ethanol (depending on the processing step) using an ultrasonic horn (model USP-600, Shimadzu, Kyoto, Japan). The features of the ultrasonic redispersion have been well-described elsewhere.[3]

The particle-size distribution was analyzed using a laser particle-size analyzer (model LSPZ-100, Otsuka Electronics, Osaka, Japan). A very small amount of powder was mixed with distilled water for the analysis.

Aqueous suspensions were prepared containing 18–20 vol.% of the Pt (or Pd)–3Y-TZP nano-composite powders by adding the dispersant [ammonium polycarboxylate (ALON A-6114), Toaghosei Co., Japan)]. Consolidations of the suspensions by slip casting and subsequent CIP at 400 MPa were applied. The relative density of the zirconia ceramic was based on 6.06 g/cm^3, and the relative densities of the composites were calculated according to the wt.% of Pt in each composite ($d = 21.09$ g/cm^3) or Pd ($d = 12.02$ g/cm^3). The samples were sintered at the temperature of 1150 °C and times ranging from 2 to 30 h in order to produce a ceramic with a highest density and the finest grain size.

Phase identification of the metal–oxide composite powders after drying and calcination was determined from X-ray diffractometry data (XRD) (Model JDX-3500, Jeol, Tokyo, Japan). Observation via TEM (Model JEM-2000-EX, Jeol, Tokyo, Japan) operated at 200 kV was used to determine the powder morphology, and the final microstructure of sintered metal-ceramic composite.

3. Results and discussion

A TEM micrograph of the 3 mol% yttria-stabilized zirconia (3Y-TZP) nano-powder is shown in Fig. 1. The primary crystallites with an average size of ~5nm are

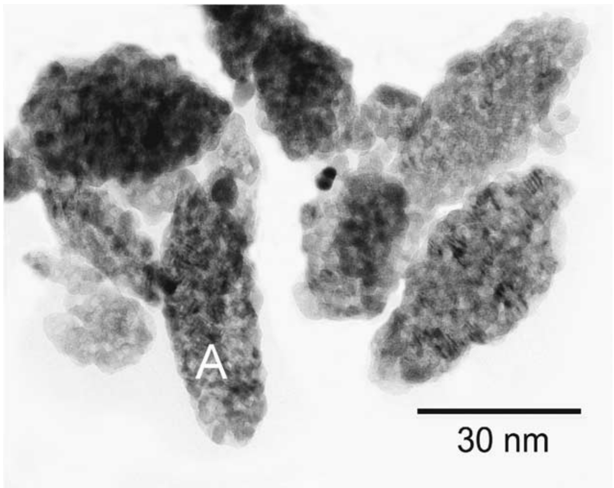

Fig. 1. 3Y-TZP porous nano-aggregates impregnated with 1.5 wt.% of platinum.

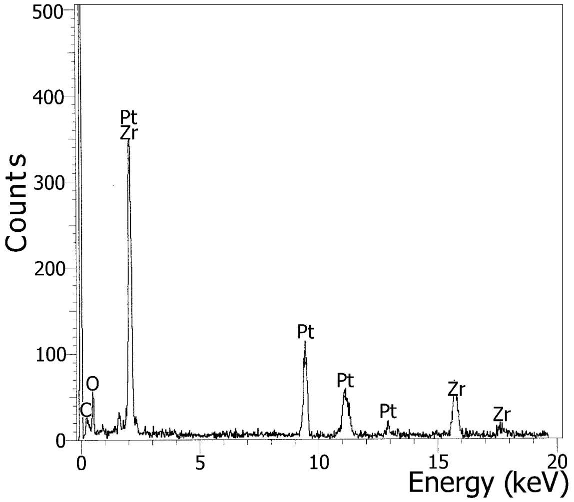

Fig. 2. TEM–EDX of nano-aggregate A on Fig. 1.

aggregated into uniformly-shaped secondary nano-aggregates with a mean aggregate size of 20–40 nm. The aqueous suspension of the 3Y-TZP powder was mixed with K_2PtCl_4 or K_2PdCl_4 and the SDS aqueous solution. Subsequent sonochemical reduction of Pt or Pd ions was applied. A significant amount of Pt (Pd) was embedded into the porous aggregates of the 3Y-TZP powder (Fig. 1).

The TEM–EDX spectra (Fig. 2) of aggregate A from Fig. 1 show the existence of platinum inside the aggregate. We can conclude from Fig. 1 that the sonochemical reduction of the K_2PtCl_4 allowed the production of uniformly shaped zirconia-based metal-ceramic nano-aggregates impregnated with platinum.

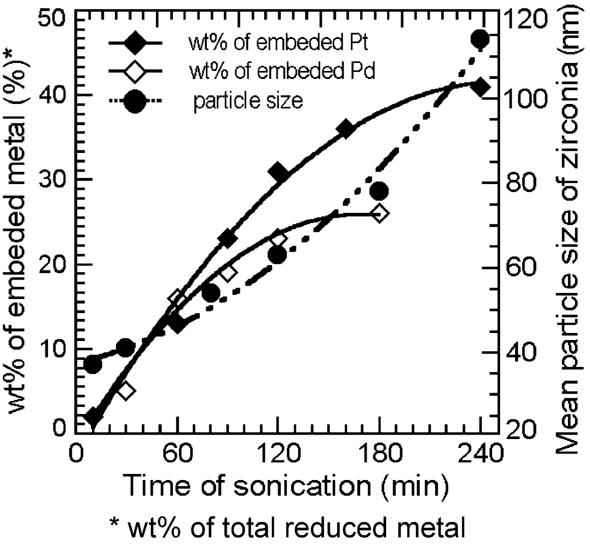

Fig. 3. The influence of the implosions of the cavitation bubbles during sonication treatment on the wt.% of impregnated platinum, and on the evolution of the mean aggregate (agglomerate) size of platinum and palladium-doped 3Y-TZP powders.

The particle size analysis (LPSA) data for the aqueous suspensions of the 3 mol% yttria-stabilized zirconia powder impregnated with 5 wt.% of platinum and 5 wt.% of palladium respectively are shown in Fig. 3. The measured initial mean aggregate size of the 3Y-TZP powder is quite small, which implies that the aggregates of the primary crystallites are very uniform and non-agglomerated. The sonochemical reduction of the platinum (or palladium) compounds was applied. The color of the mixed suspensions of the 3Y-TZP nano-powder with an aqueous solution of K_2PtCl_4 (or K_2PdCl_4) with SDS mixed with changed from yellow-white to light gray. The fine (2–5 nm) platinum or palladium particles were synthesized.

The influence of the implosions of the cavitation bubbles during sonication treatment on the wt.% of the impregnated platinum, and on the evolution of the mean aggregate (agglomerate) size of Pt- and Pd-embedded 3Y-TZP powders is shown in Fig. 3. We can assume that only around 12 wt.% of the total reduced platinum or 16 wt.% of palladium can be embedded on the surface and into the zirconia nano-aggregates during 80 min of sonochemical treatment. The rest of the platinum or palladium remained in the free state and was removed by centrifuging with a supernatant liquid. The following ultrasonic treatment allowed an increased wt.% of embedded metals. After a 120 min sonication, up to 30 wt.% of the platinum and 24 wt.% of the palladium were impregnated into the zirconia aggregates. Finally, after a 240 min ultrasonication, up to 43 wt.% of the platinum was impregnated into the zirconia aggregates.

However, at the same time, the mean particle size of the composite powder (i.e. the mean aggregate (agglomerate) size of zirconia powder) changed. After 60 min of ultrasonication, the mean size of the zirconia aggregates in the suspension changed to the 60 nm, and 72 nm after 180 min sonication (only ~35 wt.% of Pt and ~26 wt.% of Pd were bound to the zirconia within the same period). The mean particle size changes to 117 nm during the 4 h ultrasonication. In the same time, the free platinum was also aggregated.

The possible reasons why the particle size changes during the sonochemical reduction of platinum in the presence of the zirconia nanopowder are as follows. From capillary pressure arguments, the surface tension of the water is a critical component in the bonding of the neighboring particles. The capillary pressure of water for the extremely fine nano-size zirconia primary particles, which are on the order of 7±4 nm in size, is extremely high. This can explain the aggregation of the neighboring primary crystallites and agglomeration of the nano-aggregates.

The ultrasonication gradually agglomerates the powder in suspension because the multi-bubble ultrasonic cavitation generates the high temperature and pressure

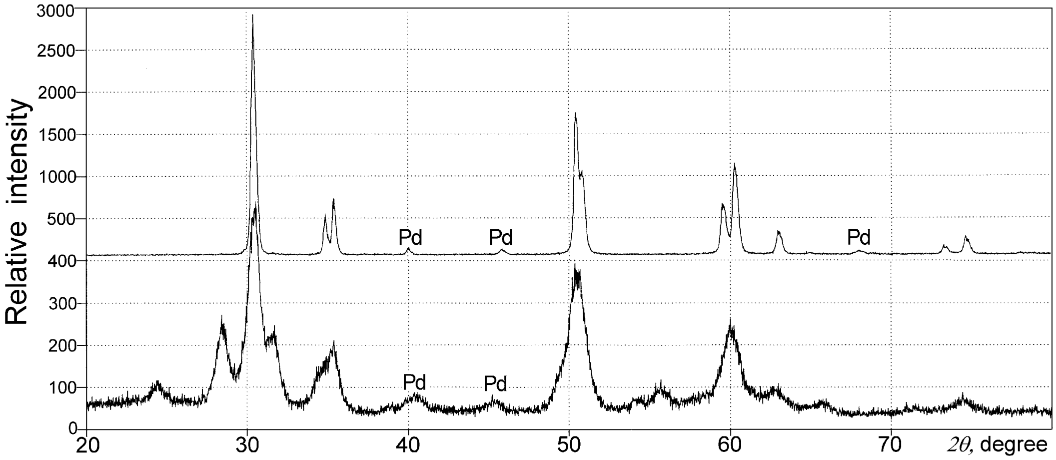

Fig. 4. The XRD pattern of the 1.5 wt.% Pd–3Y-TZP composite nanopowder. All non-specified peaks attributed to tetragonal and monoclinic ZrO_2.

of several atmospheres. As a result, solid necking of the neighboring nano-crystallites took place in the contact areas among the crystallites during the multiplied implosions of the cavitation bubbles.

To prevent such a reagglomeration route B was used. The sonication was stopped after 80 min after the color of the suspension changed from yellow-white to light gray. The beaker with the suspension was heated using the temperature-controlled heater of a magnet stirrer. After 5 h, the color of the suspension changes to dark-gray and the testing by centrifuging showed a separation of the uniform dark-gray Pt–3Y-TZP (or Pd–3Y-TZP) composite powder from the aqueous supernatant. It should be noted that the centrifuging of the suspension (3Y-TZP mixed with the platinum complex solution) sonochemically reduced for less than 80 min produces a supernatant with a pale yellow color (or bright yellow for less than 40 min of sonication). This evidence allowed us to conclude that the reduction of Pt(II) and Pd(II) ions was not complete.[13,14] On the other hand, the longer sonochemical reduction (80–120 min) gives the dark brown supernatant. That is clear proof of the completion of platinum or palladium reduction. However, in the same time, such color of the supernatant is evidence for the fact that a significant amount of platinum or palladium remained in the suspension and had not the cohesion with zirconia particles.

The X-ray diffraction pattern of the 1.5 wt.% Pd embedded 3Y-TZP composite nanopowder is shown in Fig. 4 (a). The sample for XRD analysis was of the composite powder produced by route B that had been previously washed from the residual compounds, and dried. The very wide peaks of palladium can be seen in this pattern. This figure confirmed the crystallinity of palladium after sonochemical reduction and without further calcination.

Aqueous suspensions of the Pt–3Y-TZP and Pd–3Y-TZP nano-composites with the minimum possible viscosity were prepared by changing the solid content and the amount of additional dispersant. The optimum solid contents of the 3Y-TZP nano-powder suspension were found to be 20 and 18 vol.% for the platinum and palladium composites respectively. The amount of the 4.5 wt.% dispersant was appropriate for obtaining well-dispersed suspensions from the both composite powders. At a lower or higher amount of dispersant, the suspension became too stiff for slip casting.

The isothermal sintering behavior was studied at 1150 °C. The densification, $D = 98.5\%$, was demonstrated by sintering of the Pt–3Y-TZP and $D = 99.3\%$ (Pd–3Y-TZP) at 1150 °C for 30 h.

The XRD pattern of the sintered nano-composite is shown in Fig. 4(b). The sintered Pd–3Y-TZP metal-ceramic composite showed only the XRD peaks of the fully tetragonal zirconia polycrystals and three major (111), (200) and (220) palladium peaks.

Fig. 5 is a TEM micrograph of the 1.5 wt.% Pt–3Y-TZP dense nano-grained metal-ceramic composite

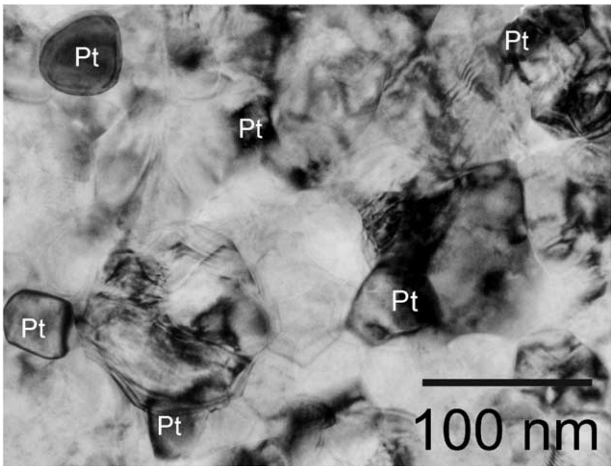

Fig. 5. The TEM micrograph of 1.5 wt.% Pt–3Y-TZP composite sintered at 1150 °C for 30 h.

sintered at 1150 °C for 30 h. The uniform distribution of the platinum grains (30–50 nm) in the zirconia matrix can be seen.

4. Conclusion

Pt and Pd nano-particles (2–5 nm) produced by sonochemical reduction were impregnated into zirconia (3Y-TZP) nano-aggregates (20–45 nm). Using the colloidal technique and low-temperature (1150 °C) sintering, we prepared the Pt–3Y-TZP and Pd–3Y-TZP (0.5–2 wt.% of platinum) nano-composites with uniform distribution of the Pt (Pd) grains and with a zirconia average grain size of 120 nm. The platinum and palladium grain size range was 20–60 nm.

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